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THE ACCURACY OF THE COMMERCIAL ASSAY FOR SILVER.[1]

BY FREDERIC P. DEWEY.

IT is generally considered that the fire assay for silver is remarkably accurate when properly carried out. Ricketts says, page 79, "The assay for gold and silver, if conducted carefully, is one of great accuracy. Duplicates of silver should agree to within one-half ounce Troy per ton" (xxx).

In general, and particularly when only small amounts of silver are present, the prevalent idea is correct, but, as shown by the above extract from Ricketts, in considering the accuracy of silver assays, too much stress is laid upon the agreement between duplicates, and I hope to show that, while the actual accuracy of the ordinary fire assay is, in many cases, very great, yet for commercial purposes still greater accuracy is required.

The main conditions which lead to accuracy are the possibility of using large quantities of material and the accuracy attainable in weighing the button, and these apply more particularly when only small amounts of silver are present. When, however, large quantities of silver are present we cannot carry on the process so successfully with so large a quantity of material, and, if we could, we might get a button too large to weigh on a button balance, and thus sacrifice some delicacy of weighing.

It has long been known that there are three sources of loss in assaying; first, from silver going into the slag; second, by silver absorbed by the cupel; third, from volatilization of silver. In dealing with rich materials corrections have been applied, and in the case of bullion it has been sought to correct for all losses by

[1] Read before the Washington Section, April 12, 1894.

6-28-94

running a check assay as near as possible like the test. When, however, we come to consider large quantities of ore, even though they carry only a moderate number of ounces of silver per ton, it is found that greater accuracy of assay for silver is necessary even for this class of material.

This is most clearly shown by a "clean-up" run by the Russell process for lixiviating silver ores. Fifty tons of ore, carrying by the ordinary assay 2,178 ounces of silver, or 43.43 ounces per ton, were treated by the Russell process, and 2,149 ounces of silver recovered, or 99.6 per cent. of the silver shown by the ore. In addition to this the tailings showed 272.25 ounces, or 12.5 per cent. Making a total of 111.5 per cent.

After a thorough investigation of this anomalous result the samples were re-assayed, but the slags and cupels were saved and also assayed, and the results added to the main assay. By this proceeding the ore showed 3.53 ounces more per ton, and the per cent. of silver saved was reduced to 91.5 per cent. Adding to this the 12.5 per cent. remaining in the tailings we have 104 per cent. The increase of silver found in the slag and cupel amounted to 8.1 per cent. of the silver in the ore, and the excess of 4. per cent. on the total may perhaps be assumed as about the volatilization loss in this case.

Attention having been called to the importance of this well-known, but hitherto unappreciated inaccuracy in silver assaying, the Russell Process Company has collected many statistics upon the subject, and I am indebted to a forthcoming pamphlet upon the subject of "plus clean-ups" for much information. I am also indebted to Mr. H. E. Wood, assayer, of Denver, Col., and to the Dewey-Walter Refining Company for many figures used in this paper.

In general, the percentage of the inaccuracy of the ordinary commercial assay varies inversely with the value of the material assayed when figured upon that value.

In order to see this most clearly it is necessary to compare results on the same class of material, and, preferably, made by the same assayer under practically constant conditions. Sometimes when a series of individual results differs irregularly, if the results are grouped considerable regularity may appear. For

instance, on looking at a series of miscellaneous results on ores running from fifteen to forty ounces per ton no regularity may appear, but if the results are grouped in periods differing by five ounces per ton they may become very regular in the variation. While different assayers working on the same material may show some regularity, they may also vary greatly.

For instance, a group of results on tailings arranged according to the increase in value by commercial assay shows as follows:

Material.	Grade. Ounces per ton.	Value commercial assay. Ounces per ton.	Value in slag and cupel. Ounces per ton.	Corrected value. Ounces per ton.	Percentage in slag and cupel.
Tailings.....	1– 3	1.8	0.5	2.3	21.8
"	"	2.8	0.4	3.2	12.5
"	3– 5	3.0	0.6	3.6	16.7
"	"	3.9	1.0	4.9	20.0
"	"	4.0	0.5	4.5	11.4
"	5– 7	5.5	0.6	6.1	10.0
"	"	6.0	1.3	7.3	17.8
"	"	6.2	1.2	7.4	16.1
"	7– 9	7.5	1.4	8.9	15.7
"	"	8.3	0.9	9.2	10.1
"	9–11	9.6	1.6	11.2	14.3
"	"	9.7	1.6	11.3	14.2
"	"	9.8	1.3	11.1	10.0
"	11–13	12.2	1.8	14.0	13.0
"	15–20	17.5	1.6	19.0	16.9
"	"	18.5	1.8	20.3	8.9

When, however, we take out of this table the results by a single assayer, we have:

Material.	Grade. Ounces per ton.	Value commercial assay. Ounces per ton.	Value in slag and cupel. Ounces per ton.	Corrected value. Ounces per ton.	Percentage in slag and cupel.
Tailings.....	1– 3	1.8	0.5	2.3	21.8
"	3– 5	3.9	1.0	4.9	20.
"	5– 7	6.0	1.3	7.3	17.8
"	7– 9	7.5	1.4	8.9	15.7
"	9–11	9.6	1.6	11.2	14.3
"	11–13	12.2	1.8	14.0	13.
"	13–20	18.5	1.8	20.3	8.9

When we group results by five ounce periods we have:

Material.	Grade. Ounces per ton.	Value commercial assay. Ounces per ton.	Value in slag and cupel. Ounces per ton.	Corrected value. Ounces per ton.	Percentage in slag and cupel.
Tailings.....	1– 5	2.8	0.7	3.5	18.
"	5–10	7.8	1.4	9.2	15.2
"	10–15	12.2	1.8	14.0	13.
"	15–20	18.0	1.7	19.7	8.6

It has been found that the character of the ore influences the results. In three kinds of ores, base, containing seventy-five per cent. sulphurets, partially oxidized, and completely oxidized, carrying from 16.5 to 34.6 ounces of silver per ton, the percentages of silver found in the slag and cupel were as follows:

Base.	Intermediate.	Oxidized.
5.7	8.2	9.8
6.8	7.8	11.3

the results on the top line being obtained by scorification and those on the bottom line by crucible assay, of the same ore in each case.

It follows then, that when ores consisting of mixtures of altered and unaltered material are considered, the proportion between these two should be known and allowed for when comparing results on similar grades of ore, if one would discover the regularity in the variation of the results.

Again, whether the ore is raw or roasted, or has been washed, influences the result, roasted ore being generally more inaccurate than raw.

A heterogeneous table of results on ores running from ten to fifty ounces per ton is as follows:

Material.	Grade. Ounces per ton.	Value commercial assay. Ounces per ton.	Value in slag and cupel. Ounces per ton.	Corrected value. Ounces per ton.	Percentage in slag and cupel.
Ore	10–15	12.5	1.3	13.8	6.4
"	15–20	17.6	1.8	19.4	9.0
"	20–25	22.4	1.9	24.3	7.8
"	"	23.1	2.0	25.1	8.0
"	"	23.8	4.8	28.6	13.0
"	"	23.9	4.5	28.4	15.8
"	"	24.1	5.9	29.7	18.8
"	"	24.3	3.3	27.6	12.0
"	25–30	26.6	2.5	29.1	8.6
"	"	27.	4.0	31.0	13.0

Material	Grade. Ounces per ton.	Value commercial assay. Ounces per ton.	Value in slag and cupel. Ounces per ton.	Corrected value. Ounces per ton.	Percentage in slag and cupel.
Ore	25–30	27.2	2.9	30.1	9.7
"	"	28.	4.6	32.6	14.1
"	"	28.4	3.	31.4	9.0
"	"	28.9	1.6	30.5	5.0
"	"	29.7	2.8	32.5	8.6
"	30–35	30.4	3.6	34.0	10.6
"	"	30.6	2.0	32.6	6.1
"	"	30.7	3.9	34.6	11.3
"	"	31.6	3.4	35.0	10.0
"	"	31.8	2.3	34.1	7.0
"	"	31.9	3.9	35.8	10.9
"	"	32.3	3.7	36.0	10.0
"	"	33.	4.1	37.1	10.8
"	"	33.1	2.8	35.9	7.8
"	"	33.6	3.2	36.8	8.7
"	35–40	36.7	3.1	39.8	7.8
"	"	36.9	3.3	40.2	8.2
"	"	37.4	4.3	41.7	10.0
"	"	37.65	2.25	39.9	5.6
"	"	38.2	2.8	41.0	6.8
"	40–45	42.1	3.	45.1	6.7
"	"	42.3	2.3	44.6	5.2
"	"	42.4	2.4	44.8	5.4
"	"	44.7	4.3	49.	8.8
"	45–50	45.5	2.4	47.9	5.0

The variation shown by the above table is very diverse, but the following grouping by five ounce periods, and according to the character of the ore, shows the inverse variation beautifully:

Material.	Grade. Ounces per ton.	Value commercial assay. Ounces per ton.	Value in slag and cupel. Ounces per ton.	Corrected value. Ounces per ton.	Percentage in slag and cupel.
Roasted ore ..	20–25	23.5	3.2	26.7	12.
" " ..	25–30	27.3	3.5	30.8	11.4
" " ..	30–35	31.6	2.8	34.4	8.1
" " ..	35–40	36.8	3.2	40.0	8.
" " ..	40–45	42.3	2.7	45.0	6.
Raw ore.....	20–25	24.2	4.6	28.8	16.
" "	25–30	27.7	3.5	31.2	11.2
" "	30–35	31.8	3.8	35.6	10.7
" "	35–40	37.5	3.3	40.8	8.1
" "	40–45	43.5	3.3	46.8	7.1
" "	45–50	45.5	2.4	47.9	5.

While the amount of silver recovered from the slag and cupel in the case of ordinary ores is small, when stated per ton of ore, yet when a year's operations, involving ten, twenty, thirty, or more thousands of tons, are considered the difference between an ordinary and a corrected assay amounts to quite a respectable sum, and becomes well worthy of consideration in these times of low prices for silver.

When we consider rich materials, such as high-grade ore and the products of the Russell process, for instance, the slag and cupel loss on a single ton becomes considerable, and with very rich products, such as lixiviation sulphides, particularly when they carry a large percentage of copper, as in the regular Russell sulphides, this loss may amount to several hundred ounces per ton. It has been customary to use the slag and cupel assay on rich products and it was employed on the "clean-up" referred to.

I am indebted to Mr. H. E. Wood, assayer, No. 1,744 Arapahoe St., Denver, Col., for a series of results on sulphides, varying from poor to rich.

The following details give the results on assaying sulphides—scorification method. 1–20 A. T. of sulphides used, and scorification slag and cupel from original assay then rescorified and cupelled with result shown. Classified according to the grade the losses were as follows:

Under	500	Average of	1 Lot	4.170	per cent.
500 to	1,000	" "	6 Lots	2.910	" "
1,000 "	1,500	" "	14 "	2.996	" "
1,500 "	2,000	" "	9 "	2.540	" "
2,000 "	2,500	" "	12 "	2.109	" "
2,500 "	3,000	" "	21 "	1.867	" "
3,000 "	3,500	" "	19 "	1.860	" "
3,500 "	4,000	" "	19 "	1.821	" "
4,000 "	4,500	" "	10 "	1.695	" "
4,500 "	5,000	" "	7 "	1.700	" "
5,000 "	5,500	" "	4 "	1.845	" "
5,500 "	6,000	" "	4 "	1.895	" "
6,000 "	6,500	" "	1 Lot	1.630	" "
6,500 "	7,000	" "	4 Lots	1.777	" "
7,000 "	7,500	" "	2 "	1.640	" "
7,500 "	8,000	" "	1 Lot	1.420	" "
8,000 "	8,500	" "	3 Lots	1.537	" "
9,000 "	9,500	" "	3 "	1.460	" "

10,500 to 11,000	Average of	1 Lot	.....	1.570	per cent.
11,500 " 12,000	" "	1 "	.....	1.340	" "
12,000 " 12,500	" "	1 "	.....	1.270	" "
17,000 " 17,500	" "	1 "	.....	1.260	" "

The average slag and cupel absorption on the 144 lots was 2.03 per cent. of the total contents.

The following table shows the results obtained on eleven lots of regular Russell sulphides when assayed by the following method:

"Weigh out one-twentieth ($\frac{1}{20}$) of an assay ton of sulphides, fifty-five grams of granulated test-lead, and two (2) to three (3) grams of fused borax. One-half of the lead is put in the bottom of the scorifier and hollowed out; the sulphides are put into the hollow and the rest of the lead poured over them; the borax is then placed on top. The assay is then conducted in the usual way. The slag and cupel shall be ground up and assayed, and the result added to the main assay."

This method is the result of a great deal of work and has been adopted as most suitable for this class of material.

In the table are given, first, the results of plain scorification assay; second, the ounces per ton found in the slag and cupel; third, the percentage in slag and cupel; fourth, the total silver found by adding the slag and cupel silver to the scorification silver by one assayer; fifth, the total silver as found by another assayer upon the same samples, and finally, the difference between the two assayers.

Ounces per ton by commercial assay.	Ounces per ton in slag and cupel.	Per cent. in slag and cupel.	Total ounces per ton.		Differences.	
1st assayer.	1st assayer.	1st assayer.	1st assayer.	2nd assayer.	Plus.	Minus.
8,675.20	144.11	1.622	8,819.31	8,782	37.31	.....
10,074.25	189.35	1.844	10,263.60	10,119	144.60	.....
10,783.35	189.	1.720	10,972.35	10,938	34.35	.....
10,902.30	194.38	1.752	11,096.68	11,220	.....	123.32
11,015.73	191.69	1.710	11,207.42	11,090	117.42	.....
11,238.40	175.22	1.535	11,413.62	11,548	.....	134.38
11,828.75	176.72	1.471	12,005.47	12,046	.....	40.53
12,566.55	199.21	1.560	12,765.76	12,821	.....	55.24
12,665.85	199.87	1.553	12,865.72	12,841	24.72	.....
13,001.65	229.84	1.737	13,231.49	13,187	44.49	.....
13,625.50	226.52	1.635	13,852.02	13,919	.....	66.98

On comparing results on individual lots considerable variation will be found between the two assayers, but on considering the total amount of silver involved the difference becomes quite small. By the first assayer these eleven lots contain 236,418.99 ounces of silver, while by the second they contain 236,483.88 ounces, the difference between the two being only 54.89 ounces. This amount is 0.0232 per cent. of the smallest total of ounces found, and 0.0095 per cent. of the weight of sulphides involved. This shows that when carefully and properly executed the method gives concordant results on averaging a sufficient number of assays.

As showing the difference which may occur by this method of assaying, besides noting the individual difference above, between the two assayers, it may be added that one of these found the following difference on assaying the same sample at different times:

No. 1..... 144 ounces per ton.
" 2..... 90 " " "
" 3..... 112 " " "

Making a difference of 527.36 in the total silver involved.

Also on a lot of sulphides containing 218,324 ounces[1] by one assayer, a second assayer obtained 0.587 per cent. less on the same samples, and in a second comparison between the first assayer and the same smelting works, representing 156,091, the difference was 1.355 per cent.

The following results were obtained in my laboratory by Mr. Charles Earl:

Total silver. Ounces per ton.	Silver in slag and cupel. Ounces per ton.	Percentage in slag and cupel.
9,156.3	244.	2.664
9,590.	257.5	2.685
9,828.2	250.	2.543
10,077.95	198.25	1.967
10,456.	266.	2.544
10,759.	244.5	2.272
10,861.5	282.5	2.6
11,700.2	198.66	1.697
12,087.8	233.3	1.93
13,804.5	250.33	1.813

[1] *Trans. A. I. M. E.*, Pamphlet Edition. Product and Economical Results of the Marsac Refinery for the year 1892, by C. A. Stetefeldt, p. 9.

In using this method Mr. Earl usually starts four assays of each sample. As he has found the charge rather destructive to scorifiers it is not unusual to lose an assay. In two sets of four results the differences between the highest and lowest individual results were 49.6 and 95 ounces per ton. In five sets of three results the differences were 36, 54, 94, 98, and 152.2 ounces per ton. As each one of a set of assays was carried through under practically the same conditions as the others these differences may seem rather high, but the total ounces represented by these seven assays by Mr. Earl was 121,346.53 ounces, while another very expert assayer by this method, working upon the same samples, found 121,446.56 ounces, showing a difference of only 99.93 ounces on the total number of ounces involved The following table shows the individual variations:

Total ounces per ton.		Differences. Plus.	Minus.
6,769	6,847	..	78
9,400.3	9,430	..	29.7
9,590	9,524	66	...
9,928	9,880	48	...
10,078	10,119	..	41
10,456	10,446	10	...
10,759	10,833	..	74

The following tables summarize a large quantity of determinations and are taken from the pamphlet by the Russell Process Company referred to:

Material.	Grade. Ounces per ton.	Value commercial assay. Ounces per ton.	Value in slag and cupel. Ounces per ton.	Corrected value. Ounces per ton.	Percentage slag and cupel.
Lead carbonate...	1– 50	5.2	0.8	6.0	15.4
" " ...	50– 100	64.8	3.2	68	5.1
" " ...	100– 500	447.6	12.4	460	2.6
Base sulphides...	100– 500	394	37	431	8.6
" " ...	500– 1,000	766	41	807	5.1
" " ...	1,000– 1,500	1,227	36	1,263	2.9
" " ...	2,000– 3,000	2,527	88	2,615	3.2
" " ...	3,000– 4,000	3,289	113	3,402	3.2
" " ...	4,000– 5,000	4,962	116	5,078	2.2
Regular sulphides	100– 1,000	493	45	5,538	8.4
" "	1,000– 2,000	1,624	83	1,707	4.9
" "	2,000– 4,000	2,807	60	2,867	2.1
" "	4,000– 6,000	5,291	98	5,389	1.8

Material.	Grade. Ounces per ton.	Value commercial assay. Ounces per ton.	Value in slag and cupel. Ounces per ton.	Corrected value. Ounces per ton.	Percentage slag and cupel.
Regular sulphides	6,000– 8,000	7,362	110	7,472	1.5
" "	8,000–10,000	8,604	128	8,732	1.5
" "	10,000–12,000	10,538	150	10,698	1.5
" "	12,000–14,000	12,842	218	13,060	1.7
" "	14,000–16,000	14,866	180	15,046	1.2
Refinery residues,	14,000–16,000	15,952	159	16,111	1.
	Fine.	Fine.	Fine.	Fine.	
Base bullion	300– 500	400	8	408	2.
Fine "	998– 1,000	987	11.5	998.5	1.2

Material assayed.	Grade of value.	Range of inaccuracy.	Average inaccuracy.
Tailings	1– 20	18 – 8.6	13.7
Washed ore.....	15– 35	13 –10.0	10.4
Raw ore.....	20– 50	16 – 5.0	9.7
Roasted ore	20– 45	12 – 6.0	9.1
Lead carbonate	50– 100	5.1– 2.6	3.8
Base sulphides	1,000– 5,500	5.0– 1.8	3.0
Regular sulphides.....	2,000–16,000	2.8– 1.2	1.7
Copper-silver bullion, 300 "fine"		2.0	2.0
Fine bullion, 999.3 "fine".....		1.1	1.1

In a number of cases the slag and cupel have been assayed separately, but there does not seem to be any uniformity of results, except that the cupel silver is generally much greater than the slag silver, although in one case they were both the same, 0.8 ounce. In a set of twenty-nine assays, running from tailings at 6.2 ounces per ton to ore at 44.7, the cupel silver varied from 0.8 to 5.4 ounces per ton, and the slag silver from 0.1 to 1.8 ounces per ton; the lowest cupel silver was on 18 ounce ore and the highest on 24.1 ounce ore; the lowest slag silver was on 26 ounce ore, and the highest on 32.4 ounce ore, and both these assays were made by the crucible method. In only two cases was the cupel silver less than 1 ounce per ton, and one of these was on the 6.2 ounce per ton tailings, and in only two cases was the slag silver over 1 ounce per ton.

In the case of the nearly proof silver produced at the Marsac refinery, by the writers process, the straight assay shows 987 fine, corrected for slag and cupel absorption it becomes 998.5 fine, as given in the table, while with a check assay to correct the volatilization loss it becomes 999.3 fine.

When we come to consider the percentage of inaccuracy when figured upon the total material assayed we find that it is somewhat irregular but generally it follows the silver contents of the material, and in the case of rich products, becomes very large. Thus, in 2.3 ounce tailings the silver equals 0.0079 per cent. of the total and a 21.8 per cent. loss on this equals only 0.0017 per cent. of the total. On the other hand, in a 17,500 ounce sulphide the silver equals 60 per cent. of the total, but the comparatively small loss of 1.26 on this equals 0.756 per cent. of the total.

The following table gives a few results upon this point:

Material.	Grade. Ounces.	Silver per cent. of total.	Inaccuracy per cent. of silver.	Inaccuracy per cent. of total.
Tailings.....	2.3	0.0079	21.8	0.0017
Ore	20.3	0.0696	8.9	0.0062
"	30.5	0.1011	5.	0.0051
"	31	0.1063	13.	0.0138
"	49	0.1680	8.8	0.0148
Base sulphides ...	431	1.477	8.6	0.12602
" " ...	5,078	17.41	2.2	0.38302
Regular sulphides	5,538	18.98	8.4	1.59432
" "	10,698	36.33	1.5	0.54495
" "	15,046	51.58	1.2	0.61896
" "	17,500	60.00	1.26	0.756

The question is sometimes asked if some wet method would not be better than fire assaying, but at present no such method is available.

While the correction for slag and cupel loss is easily made, and ought always to be made when accurate statistics are kept, there is yet the volatilization loss to correct, and some means of doing this is very desirable. While a check assay answers very well for bullion it would hardly be possible to construct check material for the varying characters of ores and products ordinarily met with.

As chemists we should all be interested in attaining the highest accuracy possible in our analytical work, but in this case, aside from the question of accuracy, and also the money value of the silver involved, when many thousand tons of ore are considered, this point has a very important practical application in indicating and bringing out unsuspected losses in mill opera-

tions. For instance, in one case, by ordinary assays of the ore, the mill showed to be extracting 87 per cent. of the silver in the ore, which was considered good work. Corrected assays of the ore showed, however, that the extraction was only 79.3 per cent. This led to an investigation, which showed that there was a volatilization loss of 10.9 per cent. in roasting the ore. This has been cut down to 5 per cent., with the expectation of reducing it still more.

In another case the extraction plus the tailings silver was 102.7 per cent., but corrected assays showed it to be only 87.1 per cent. This was brought up to 97 per cent.

These figures show that the commercial assays of ores are too unreliable if accurate mill statistics are desired.

THE ACHIEVEMENTS AND AIMS OF PHYSICAL CHEMISTRY.[1]

By J. E. Trevor.

Received June 7, 1894.

CHEMICAL changes, in common with all other natural processes, are in their ultimate nature transformations of energy. The study of chemical processes is therefore a study of the energy phenomena which they involve. Chemical reactions may absorb or take up heat, changes of density may occur whereby work is done, electrical energy and radiant energy may be produced. But the mutual relations of heat, work, electricity, and the like, involving the characteristic factors, temperature, pressure, tension, force, potential, etc., form the subject-matter of the science of Physics, and hence it is that the study of chemical processes as such has come to be known as the *Physical Chemistry*. The object of this branch of science is to discover the simple relations connecting the various types of chemical phenomena, and to make of these relations a coherent whole.

The Physical Chemistry is a new science. Up to eight years ago nothing serious had been attempted in the way of generalization. Very important discoveries had been made before that time it is true, yet they where of a wholly disconnected character and their bearing upon a general theory of chemical processes

[1] Read before the Midwinter Fair Congress of Chemists at San Francisco, June 7, 1894.

was not seen. Prominent among these achievements of a generation whose efforts have now become history stand the experimental work of Thomsen and Berthelot in thermo-chemistry, the investigations of Kopp in stoichiometry, the dissociation theory of Horstmann and of Gibbs, the brilliant researches of Helmholtz in electro-chemistry, and that flash of insight which led to the discovery of the law of mass action. Nor is the present generation proving itself unworthy of this inheritance of scientific achievement; the chemical equilibrium, the electro-chemistry, and the thermodynamical generalizations of to-day are supplying a fit sequel to this story of the past.

In 1886 appeared van't Hoff's first paper upon the theory of solutions. It was immediately followed by that extended series of monographs, written by such men as Ostwald, Nernst, Arrhenius, Planck, Riecke, and many others, which has made the thermodynamical theory of solutions one of the most remarkable conquests of the science of chemistry. Van't Hoff's discovery that the inner energy of a dissolved substance when dilute is independent of the volume of its solution led at once to the discovery of simple relations between the physical properties of solutions and their molecular concentrations, *i. e.*, to a series of novel methods for the determination of molecular weights; it brought about an unforeseen extension of the law of mass action to the solution-equilibria of both homogeneous and heterogeneous systems; it led to a strict formulation of the influence of temperature upon chemical equilibrium and the velocities of reactions, to a mathematical theory of hydrodiffusion, to a comprehensive theory of concentration currents and of the voltaic cell, and to an unexpected culmination of Ostwald's exhaustive investigations upon the chemical affinities of aqueous acids and bases. This breathless succession of advances constitutes one of the most interesting and exciting chapters of the history of chemical theory.

It is being succeeded at the present time by work of a more general and wide-reaching character. The great generalizations of thermodynamics are hastening the day when chemistry shall become a deductive science. Planck, of Berlin, has recently directed especial attention to the following course of reasoning.

There are certain processes, such as the conduction of heat from a hot to a cold body, or the diffusion of a dissolved substance from a high concentration to a lower one, which are irreversible—they take place only in one direction. This fact may be shown to require the conclusion that the general trend of natural processes is in an assignable direction; the general state of things tends all one way. If this were not so it would be possible to reverse history, to make trees grow down into seeds, and to awaken fossils to quivering, pulsating life.

The strict formulation which represents this general tendency furnishes, therefore, a means of determining definitely the direction which any given natural process, chemical or otherwise, must pursue; and it leads in consequence to an exact relation between the energy factors upon which the final state of the material system concerned is made to depend, a relation which combines in one expression every law of chemical equilibrium. From it can be derived in order all the laws of isothermal chemical equilibrium in homogeneous and in heterogeneous systems, and those which represent the effect of changes of temperature and of pressure in displacing such equilibria; it yields further the laws relating to the many physico-chemical properties of solutions which depend upon the vapor pressures; and it furnishes, finally, the almost numberless theorems of electro-chemistry. Thus it is seen that from the assumption of a simple fact of experience, the irreversibility of heat conduction, a mathematical theory of chemical changes is obtained which organizes into a coherent and logically connected whole all the exact relations of chemical science. The deductive value of this theory is enormous, in that it clearly points out the limits of our knowledge in every direction. And for the reason that the system is uniform and falls into a logical order it becomes of the greatest service in aiding the conception of chemical theory as a whole and in fixing in the mind the relations between its parts.

Another form of the same fundamental idea has been employed by the eminent French mathematical physicist, Duhem, in developing a systematic treatment of the theory of chemistry. From the properties of his *thermodynamical potential* (taken from the thermodynamical studies of Willard Gibbs) he has evolved

an orderly discussion of the theory of dissociation, the continuity of the liquid and gaseous states, and the general theory of the chemical and physical equilibria of fluid mixtures, all of which is characterized throughout by strict uniformity of method and an unusual elegance of mathematical style.

These two methods of research are essentially identical, for they are based upon the same principle, and they both refer the solution of every problem to the properties of a single function of quantities which fix the state of the system concerned. In this respect they mark a distinct advance in the study of the science of chemistry.

The eminent fruitfulness of these thermodynamical methods has led to a fuller appreciation of the bearing and significance of the great energy generalization which they involve, and upon which, indeed, the entire framework of modern physical science really rests. If chemistry be in its ultimate nature, an energy science, chemists obviously must study those energy transformations which constitute its phenomena. In a chemical change different energies come into play, and the change continues until they hold one another exactly in balance. This balance determines, therefore, what the final state of the system in question shall be. Two energy forms are in equilibrium when a possible variation of one is exactly compensated by the corresponding variation of the other. All that is necessary then to determine the final state which any given material system must assume is to represent mathematically the possible variations of its opposed energies and to set these variations equal. This procedure is identical with that which is employed in Statics to investigate the equilibria of mechanical systems. When applied systematically to the different types of chemical action it yields a rational classification of chemical processes, and, in a logical sequence, all of the known elements of the modern physical chemistry. This reconstruction of theoretical chemistry upon the basis of the Energy Theory is one of the most brilliant of Ostwald's many splendid contributions to science.

It is important to observe that the great advances of recent years in the theory of chemical action have not been made with the aid of the kinetic-molecular hypothesis. The assumption of

atoms and molecules has been a constant hindrance to the progress of rational chemical theory. The "Kinetic Theory of Gases" has been able to account for the behavior of gases only in an imperfect manner, and it has not been able to account at all for the laws of chemical equilibrium and the properties of solutions. The fact that gases react in simple volume relations justifies the selection of a definite volume as the chemical unit, the relative weight of this volume becoming then the so-called molecular weight, but it justifies in no wise the conclusion that gases are composed of discrete particles. This unwarranted assumption was made because of a desire to "explain" from the behavior of a purely mechanical system the observed characteristics of gases. Yet the behavior of the model is, after all, only approximately that of the gas. And, moreover, it is not the province of science to "explain" anything, certainly not to explain phenomena by reference to irrealizable mechanical constructions. It is becoming more and more clearly seen, day by day, that the business of science is to *describe* phenomena in a simple manner, to seek actual relations between measurable quantities, to deal only with things which can be handled and observed. Hypotheses must be employed, if at all, only provisionally and as analogies.

There is no desire to deny that the molecular hypothesis has been fruitful of results; any hypothesis may lead to work whereby knowledge is gained. Yet this one has nearly outlived its usefulness, and it will be employed less and less in the future by those chemists who refuse to believe upon insufficient evidence. As an accepted hypothesis its days are numbered. In the place of the Molecule appears the Molecular Weight, a sharply defined quantity whose conception does not transcend experience.

The average student of chemistry is trained to confuse the real with the hypothetical. He believes molecular formulas and molecules to involve each other, whereas, the former represent facts while the latter are creations of fancy. The molecular formulas of our chemical equations possess a very real and important signification, and this is no less true of the structural formulas which form at the present time so important a feature of the technical apparatus of organic chemistry. These structural formulas

are valuable mnemonic expressions for the individual chemical character of the substances in question, and when employed for what they represent their value is not to be underestimated. Yet one must not for a moment suppose that they supply a picture of the mechanical structure of small particles of the substances; this idea is a purely hypothetical one, and at the best represents nothing more than the original facts. The symbols, properly used, represent the facts and not the hypothesis.

The general methods which give to the best modern thought its distinctive character appeal to experience alone. Things other than observable fact do not fall within their province, such things are not objects of human knowledge. It should not need emphasis that this is the only natural and reasonable basis for a science of the facts of nature. And it cannot be denied that our first real insight into the nature of chemical processes has been gained by the application of these straightforward methods.

The age of mechanical hypotheses is of the past. The desire to replace known laws by unproven or unprovable assumptions is passing away. And it can now be clearly recognized that the view which seeks to place mechanics at the base of all departments of physical science is, in its thoughtless exclusion of energies other than mechanical, a prejudice. Now, the thermodynamical systems and the energy doctrine involve only accessible facts. They are built upon no assumption other than the irreversibility of some spontaneous process, or the observed conservation of the energy of an isolated system. Their aim is to increase knowledge, and not representations of knowledge, to seek out the facts of nature and the wonderful and simple relations subsisting among these facts. And in this there are notable instances of what is fittingly termed *Physical Theory*. The distinction between theory and hypothesis can now be sharply drawn, the Hypothesis is a mechanical construction substituted by the imagination for things as they actually are, the Theory is an organized system of logical consequences drawn from the established facts of experience. Mechanical Hypotheses have dimmed the glory of the history of chemistry, Physical Theory endows chemistry with the attributes of an exact science.

The subject of electro-chemistry has become, in recent years, a

prominent feature of the physical chemistry. The energy liberated in chemical changes may appear as electrical energy; or electrical energy may, during a chemical process, be transformed into the inner energy of the products of the reaction. Our knowledge of these things has had a contentious and a profoundly interesting history. The strugglings and gropings of a hundred years lie between this time and that in which the first observations of electro-chemical action were made by Galvani and Volta. The intervening years have been largely occupied by a study of the phenomena of electrolysis pure and simple. The insight thereby gained into the nature of this process has led to a clear conception of what takes place in the various types of voltaic cell, and has, in consequence, rendered accessible to immediate calculation all the essential details of the transformation between the free energy of the chemical action in a cell and the electrical energy which is produced. This comprehensive theory of electro-chemistry is one of the greatest results which has followed the introduction of the energy theory into chemistry, it is the fitting close of a century of effort.

And now that such a result has been reached it is a matter for congratulation that the event is to be marked by a great literary monument. This is Ostwald's work on electro-chemistry, at the present moment passing through the press, a book which is to give a full and clear account of the entire development of the subject from its beginnings.

The influence which has been exerted upon physical chemistry by its literature is of the most interesting character. Widespread interest in physical chemistry as an independent subject dates, probably, from the publication of Ostwald's *Lehrbuch der allgemeinen Chemie*, in 1887. The interest thus aroused was immediately intensified by the appearance of van't Hoff's thermodynamical theory of dilute solutions, and the remarkable series of theoretical and experimental discoveries which followed in its train. This period marks, undoubtedly, the beginning of physical chemistry as a connected and organized science. Its development since then, due to no small extent to the efforts of Ostwald and van't Hoff and their pupils, has found a fit channel for expression in the pages of the *Journal of Physical Chemistry*

(*Zeitschrift für physikalische Chemie*), whose first number appeared also in 1887. A systematic account of the present status of the science is now being supplied by a new edition of Ostwald's *Lehrbuch*, which has in the meantime grown to be a monumental work in three volumes, two of which are already in print. And it is well to add that the general desire for a text-book of less exhaustive nature has been well met by the briefer "*Outlines*" by the same author, and the "*Theoretical Chemistry*" of Nernst. Due reference has been already made to Ostwald's magnificent publication upon electro-chemistry.

The great demand now to be made upon the future is for a book upon the *General Theory of Energy;* a work in which the relations of natural phenomena to one another may be brought into a clear light, a work in which we may finally see effaced the artificial distinctions between the subjects of Chemistry, Mechanics, Thermodynamics, Electricity, etc., which, as we have them now, are partly historical, partly physiological, partly conventional, and wholly unsatisfactory.

The science of Physical Chemistry is, at the present moment, in a stage of the most active development. Every month brings to the light some startling experimental discovery, or some broader generalization. The general methods now in use have already begun to furnish a complete thermodynamical theory of solutions for all concentrations, a thorough grasp of the conditions of chemical equilibrium in complex heterogeneous systems, a really adequate comprehension of the phenomena of galvanic polarization, and an exact definition of chemical affinity. These are the things of to-day, what the morrow may bring forth is for no man to say. Yet it is certain that the chemistry of the future will deal with fact and not with fancy, and that its immediate aim will be the establishment of exact relations between those quantities upon which the state of every material system ultimately depends. For it is in this way, and in this way only, that a real insight into the nature of chemical processes will finally be attained.

CORNELL UNIVERSITY,
May, 1894.

PROTEIDS OF THE WHEAT KERNEL.[1]

By Thomas B. Osborne and Clark L. Voorhees.

THE importance of wheat as a breadstuff, and the fact that its superiority over all other cereals for bread-making mainly depends on the properties of the proteids composing the gluten which wheat dough yields when cautiously washed with water, justify giving here in some detail an account of the present state of knowledge regarding the proteids of wheat.

The wheat used in our work was of two kinds. One of these, Scotch Fife, a hard spring wheat, raised in Minnesota, was obtained through the kindness of Dr. D. N. Harper, late chemist of the Minnesota Experiment Station. It was carefully selected, free from all other varieties, and was milled under the supervision of Dr. Harper, who supplied us with samples of the various mill products, together with some of the unground wheat. Two grades of flour were used; namely, "patent flour," made from the finest and purest middlings, and "straight flour," from the coarser and less pure middlings. The "shorts," chiefly composed of the outer coating of the seeds together with adhering portions of the endosperm, was also examined. Samples of whole wheat flour were prepared as required from the wheat by grinding small quantities in the laboratory mill. The other wheat used was a variety of winter wheat known as "Fultz." This was procured from Mr. F. S. Platt, seedsman, of New Haven, and was carefully selected and freshly harvested.

When wheat flour or meal is made into a stiff dough with water and then carefully kneaded or squeezed in a gentle stream of water, the starch which makes up 60–68 per cent. of the flour or meal is gradually washed away for the most part, and there remains a tough elastic sticky mass.

The first published description of this body was made by Beccari in 1745 who gave it the name it still bears; *viz.*, *Gluten*.

In 1805 Einhof observed that hot alcohol extracts from wheat flour a substance resembling gluten. In 1820 Taddei showed

[1] First printed in the Report for 1893 of the Connecticut Agricultural Experiment Station, New Haven; communicated by the author.

that gluten contains two substances, one soluble the other insoluble in boiling alcohol.

Since 1820 many chemists have undertaken to investigate gluten but their conclusions as regard the number, properties and composition of the proteids it contains, are extremely discordant. Einhof, Boussingault, Bouchardat, Denis, Weyl and Bischoff and Martin have considered gluten to consist essentially of a single proteid. Berzelius, DeSaussure, Liebig, Dumas, and Cahours, and Von Bibra, believed it to contain three, while Ritthausen and Bechamp regard it as composed of four proteids.

We have separated from the wheat kernel five distinct proteids; *viz.*, Gliadin, Glutenin, a Globulin, an Albumin and a Proteose. A proteose-like body, apparently distinct, was also obtained, but in too small quantity for satisfactory examination.

The mode of isolating these substances in a state of comparative purity and establishing their individuality, is fully stated in a former paper,[1] to which reference must be made for details.

Of these proteids only the first two properly belong to gluten.

I. *Gliadin* is the proteid which is readily dissolved from wheat flour and from gluten by hot dilute alcohol. It also exists in the rye-kernel.

This substance when dehydrated by absolute alcohol and thoroughly dried over sulphuric acid, forms a snow-white, friable mass which is easily reduced to a powder. If dried after being moistened with dilute alcohol or water it resembles, in appearance, pure gelatin. Dried thus, in thin sheets it is perfectly clear and transparent but is rather more brittle than gelatin. When treated in the cold with distilled water it becomes sticky and slightly dissolves. If the water is warmed, more dissolves and on boiling, much goes into solution. Solutions in warm water on cooling, deposit a part of the substance. The solution in pure water is instantly precipitated by adding a very minute amount of sodium chloride.

In absolute alcohol gliadin is entirely insoluble, but dissolves on adding water, the solubility increasing with the addition of water up to a certain point, and then diminishing. The exact degree of solubility for various strengths of alcohol has not been

[1] *Am. Chem. J.*, 15, 392.

determined, but mixtures of about seventy per cent. of alcohol and thirty per cent. of water dissolve the proteid in almost indefinite amount. From solutions in strong alcohol as well as from those in very weak alcohol the proteid is precipitated by adding a few drops of solution of sodium chloride, the completeness of precipitation depending on the strength of the alcohol and the amount of salt added. The more the alcohol varies in strength from seventy to eighty per cent. the more completely is the substance precipitated.

In extremely dilute acids and alkalies this proteid is readily soluble, and is precipitated from such solutions on neutralization apparently unchanged either in properties or composition.

Gliadin gives with Millon's reagent, with nitric acid and with the biuret-test, the usual proteid reactions. Dissolved in concentrated hydrochloric acid, a beautiful violet color develops slowly. With warm fifty per cent. sulphuric acid a similar color appears which is greatly increased in intensity on boiling.

On boiling its aqueous solutions, gliadin coagulates and becomes insoluble both in alcohol and in 0.2 per cent. potash solution, but is not thus converted into glutenin, the latter being soluble in weak alkali.

Gliadin was so called by Taddei because of its resemblance to glue. It has also been called plant-gelatin by Liebig, and glutin by Dumas. The plant-casein of Dumas, the mucin of De Saussure and Berzelius, the gluten-fibrin and wheat-mucedin of Ritthausen, are impure gliadin.

Gliadin is entirely distinct in composition from the alcohol soluble proteids of barley, maize, and oats. We found in Fife wheat, 4.33, and in Fultz, 4.25 per cent. of gliadin.

Our analyses of these gluten proteids are as follows:

	Gliadin of wheat, average of twenty-five analyses.	Gliadin of rye, average of thirteen analyses.	Glutenin of wheat, average of eight analyses.
Carbon	52.72	52.75	52.34
Hydrogen	6.86	6.84	6.83
Nitrogen	17.66	17.72	17.49
Sulphur	1.14	1.21	1.08
Oxygen	21.62	21.48	22.26
	100.00	100.00	100.00

II. *Glutenin.* Characteristic reactions of a proteid body which

can be dissolved only in dilute acids or alkalies are necessarily very few in number. Our preparations of glutenin after drying over sulphuric acid, were found to yield to distilled water, especially when warm, a little proteid substance. Diluted alcohol also dissolved a minute amount of proteid matter in the cold, and when heated to boiling, a much greater quantity. It is questionable whether the substance dissolved by water and by alcohol was not a trace of gliadin which had failed to be completely extracted in the process of preparing the glutenin. The fact that the solution in hot alcohol began to precipitate at once on cooling, and that especial care had been taken in every case to remove the gliadin, makes it probable that glutenin is slightly soluble in water and in alcohol, especially if these are warmed.

In very dilute alkalies, as 0.1 per cent. potash solution, and in very dilute acids, as 0.2 per cent. hydrochloric acid, glutenin, after dehydration with absolute alcohol and drying over sulphuric acid, is slowly soluble, with the exception of a greater or less amount of coagulated residue, depending on the circumstances of its preparation. When freshly precipitated, and in the hydrated condition, it is extremely soluble in the slightest excess of caustic alkali, and in a somewhat greater but still very slight excess of acid. In this condition it is also soluble in the slightest excess of sodium carbonate solution or ammonia. After drying over sulphuric acid it dissolves partly in 0.5 per cent. sodium carbonate solution.

Dissolved in concentrated hydrochloric acid it gives a solution slightly yellowish at first, but becoming a deep violet color on standing. In sulphuric acid diluted with an equal volume of water the solution is brownish in color after boiling, and remains clear when diluted. The undiluted solution, on standing, retains its brown color.

A comparison of the analyses of glutenin with those of gliadin shows a very close agreement of the two in composition. As it is well known that many proteids readily lose their solubility without change of composition detectable by analysis, it might seem proper to consider this body as an altered and insoluble gliadin.

There is, however, no evidence that gliadin is actually trans-

formed into glutenin, and since very recent investigation shows that rye-grain contains gliadin, but probably not glutenin, it would appear that the two are to be regarded as distinct.

This proteid, in an impure state, has been termed by various investigators zymom,* plant-fibrin, gluten-casein, and gluten-fibrin. As all these names are associated with confused and erroneous notions as to its composition, origin, and properties, they are all properly discarded in favor of the new designation, glutenin.

In Fife wheat we found 3.96, and in Fultz, 3.91 per cent. of glutenin. The other proteids in the wheat kernel are—

III. *Edestin*,[1] a *globulin* belonging to the vegetable vitellins, soluble in saline solutions, precipitated therefrom by dilution, and also by saturation with magnesium sulphate, or ammonium sulphate, but not by saturation with sodium chloride. Partly precipitated by boiling, but not coagulated at temperatures below 100°. The wheat kernel contains between 0.6 and 0.7 per cent. of this globulin. When dried at 110° its composition was found to be as below stated.

IV. *Leucosin*,[2] an *albumin*, coagulating at 52°, unlike animal albumin in being precipitated on saturating its solutions with sodium chloride or magnesium sulphate. It is not precipitated on completely removing salts by dialysis in *distilled* water. It was found to form between 0.3 and 0.4 per cent. of the wheat kernel, and to have the following composition when separated from solution in the coagulated form by heating to 60° C.:

	Edestin.	Leucosin, coagulated.	Coagulum from proteose.
Carbon	51.03	53.02	51.86
Hydrogen	6.85	6.84	6.82
Nitrogen	18.39	16.80	17.32
Sulphur	0.69	1.28	24.00
Oxygen	23.04	22.06	
	100.00	100.00	100.00

V. A *proteose*, precipitated (after removing the globulin by dialysis, and the albumin by coagulation) by saturating the solution with sodium chloride, or by adding twenty per cent. of sodium chloride and acidifying with acetic acid. This body was

[1] Ἐδεστὸς edible.

[2] Λευκὸς white.

not analyzed in its unaltered form. On concentrating its solutions by boiling, a *coagulum* was gradually developed which formed about 0.3 per cent. of the wheat kernel and had the composition given above.

VI. The solution filtered from the substance just described (V.) still contained a *proteose-like body* which was not obtainable in a pure state. Its amount could only be roughly estimated by precipitating the concentrated filtrate from the preceding substance with alcohol, and multiplying the nitrogen contained in the precipitate by 6.25. The amount of this proteose was from 0.2 to 0.4 per cent. of the seed. Both this proteose and the above coagulum are unquestionably derivatives of some other proteid in the seed, presumably the proteose first mentioned.

The Formation of Gluten.—Wheat, as far as is known, is the only plant whose seeds contain proteid matter separable in a coherent form from the other constituents by washing with water. When ground fine and mixed with a suitable quantity of water it yields a dough from which a light, porous bread can be made. The importance of this fact in bread-making is so great that considerable attention has been paid to gluten by the chemists who have studied wheat proteids.

The investigations of Günsberg and of Martin, as well as our own, disprove the existence of gluten-fibrin and mucedin, which are currently stated to exist in gluten, and demonstrate that, as Taddei maintained, gluten consists of two proteids only.

Weyl and Bischoff have asserted[1] that the proteid matter of the wheat kernel is *chiefly a globulin substance*, and that in contact with water it undergoes a change, presumably through the influence of a ferment, by which gluten is first produced.

The statements of these investigators are not sustained by any sufficient evidence. They say: "On investigating the proteids of wheat meal, one of us found principally a globulin substance, which he designated, in consequence of its similarity to myosin of the muscle, *vegetable myosin*. This vegetable myosin must be the mother-substance of the gluten, since in the wheat meal, together with it, other proteids, if at all, exist only in very small amount." What the reasons were for concluding that the

[1] *Ber d. chem. Ges.*, 1880, 367.

"myosin" constitutes nearly, if not all, the proteid of the wheat kernel does not appear. In view of our results this statement is certainly erroneous. Direct treatment of the meal with alcohol yields extracts containing gliadin in exactly the same amount as obtained from the gluten made from an equal quantity of flour, and extraction of either flour or gluten with alcohol, after complete exhaustion with sodium chloride solution, also gives the same proportion of gliadin. This substance must therefore exist in the seed, having the same composition and properties as in the gluten, and as it forms one-half of the gluten, it leaves the other half only as possibly derived from a globulin body through the influence of a ferment. If Weyl and Bischoff's view were correct, treatment of the flour with ten per cent. salt solution ought to alter the character and quantity of the gluten obtained, if not altogether to prevent its formation. This is not so, for the usual amount of gluten can readily be obtained from flour made into dough with ten per cent. sodium chloride solution, and then washed with the same until starch is removed.

Weyl and Bischoff next state that, "with the aid of a fifteen per cent. rock salt solution the flour was extracted until no proteid could be detected in the extract; the residue of the meal kneaded with water then gave no gluten. *If the globulin substance be extracted, no formation of gluten takes place.*" We have found that this is true if the flour is stirred up with a large quantity of salt solution, extracted repeatedly with fresh quantities of the same solution until no more proteid is dissolved, and the excess of solution removed by allowing the residue to drain on a filter as completely as possible. If, however, wheat flour is mixed at first with just sufficient salt solution to make a firm dough, this dough may then be washed indefinitely with salt solution, and will yield gluten as well, and as much, as if washed with water alone. This difference is due to the fact that when large quantities of salt solution are applied at once, the flour fails to unite to a coherent mass and cannot afterwards be brought together, as is possible when treated with smaller quantities of solution.

Weyl and Bischoff compare the formation of gluten to that of blood-fibrin from fibrinogen under the influence of a ferment.

They say that the formation of gluten is affected by all the conditions which interfere with the activity of ferments in general. "Large amounts of salt hinder the formation of gluten. Sulphates of magnesium and sodium behave like common salt." These statements are explained by what has been said above.

They tried unsuccessfully to obtain the supposed ferment in the following manner:

"We allowed meal with an equal weight of ninety per cent. alcohol to stand in closed vessels different lengths of time (in one case four months, then several times three to four weeks, frequently only eight to ten days). The vessels were repeatedly shaken and the yellow-colored alcoholic extract was poured off. The residue was freed from alcohol by pressing and evaporating at the ordinary temperature. After it was stirred up with water little or no gluten was obtained. Evidently the globulin substance had been coagulated for the most part by the alcohol." It is clear that if the flour were thus treated, the greater part of the gliadin would be removed. We have found that if flour be extracted with dilute alcohol until the gliadin is removed, and the residue freed from alcohol by exposure to the air, the latter will then yield no gluten when treated with water.

More recently Sidney Martin has advanced a somewhat similar theory of the formation of gluten from the proteids contained in the seed. He states[1] that alcohol extracts from gluten but one proteid substance; that this is soluble in hot water, but not in cold, and he therefore calls it an *insoluble phytalbumose*.

The residue of the gluten not dissolved by alcohol is uncoagulated proteid, if the alcohol has not been allowed to act too long. This substance he names *gluten-fibrin*. Martin further says that gluten dissolves almost completely in 0.2 per cent. hydrochloric acid, or 0.2 per cent. potash solution, leaving a small residue of fat. The solution gives a copious precipitate when neutralized, but the supernatant liquid still contains a quantity of proteid, which is the dissolved insoluble albumose. The whole of the gluten-fibrin is reprecipitated by neutralization, that is, it is wholly converted into an "albuminate."

Martin then asks: "Does flour contain gluten-fibrin? Does it

[1] *British Medical Journal*, 2, 104, *1886*.

contain insoluble phytalbumose?'' The first question he says can not be answered directly. ''The second is answered by extracting flour with seventy-six to eighty per cent. alcohol. This ought to contain the insoluble albumose if it were present as such in the flour, *but it does not contain it;* it extracts only fat.'' This statement is contrary to our experience, for we have never failed, in many experiments, thus to extract this substance (gliadin) from the flour, and that too in the same amount and of the same properties and composition as from the gluten.

Martin concludes that insoluble albumose is not present as such in the flour. He then says: ''Before proceeding to mention its precursor, it will be well to state that ten per cent. sodium chloride solution extracts from flour a large quantity of globulin and of albumose. This globulin is of the myosin type, coagulating between 55° and 60° C., and precipitated by saturation with sodium chloride and ammonium sulphate. Both the globulin and albumose are present in a much smaller quantity in the watery extract of the flour.'' From this it is evident that Martin has fallen into the same error as Weyl and Bischoff, mistaking the albumin for a myosin-like globulin, and being greatly misled as to its amount.

Continuing, Martin says: ''The direction of the evidence is to show that the insoluble albumose is formed from the soluble. Moreover, I think that the globulin is transformed into the gluten-fibrin, for I have been able to obtain from the globulin in solution a body having the same reactions as the gluten-fibrin.'' What this evidence is, which, by its direction, shows that the insoluble albumose is derived from the soluble, is not clear, and Martin makes no further statements on this point. That a body should be obtained from the solution containing the globulin which had the same reactions as the ''gluten-fibrin'' is not surprising, for the so-called ''albuminates'' derived from nearly all globulins have no characteristic reactions, being merely soluble in dilute acids and alkalies, and precipitated by neutralization in the same way as ''gluten fibrin.'' Martin then states his theory of the formation of gluten in the following scheme:

$$\text{Gluten} = \begin{cases} \text{Gluten-fibrin} & \text{—precursor, globulin.} \\ \text{Insoluble albumose—} & \text{“} \quad \text{soluble albumose.} \end{cases}$$

This can not be a correct representation of the formation of gluten, for it has been shown to be founded on two erroneous observations: First, that alcohol does not extract proteid matter from the flour when applied directly, and second, that at least one-half the proteid matter of the seed is a myosin-like globulin.

The results obtained by us, and described at length in our paper,[1] lead to the conclusion that no ferment action is involved in the formation of gluten; that but two proteid substances are contained in the gluten, gliadin, and glutenin, and that these exist in the wheat kernel in the same form as in the gluten, except that in the latter they are combined with water in an amount equal to about twice the weight of the water-free proteids. The reasons for this opinion are, first, that alcohol extracts the same gliadin in the same amount, whether applied directly to the flour, to the gluten, or to the flour previously extracted with ten per cent. sodium chloride solution; second, that 0.2 per cent. potash extracts glutenin of uniform composition and properties from flour which has been extracted with alcohol or with ten per cent. sodium chloride brine and then with alcohol, as well as from gluten which has been exhausted with alcohol.

Both glutenin and gliadin are necessary for the formation of gluten, as shown by the three following experiments:

1. A portion of flour was washed completely free from gliadin by means of alcohol of 0.90 sp. gr., next with stronger alcohol, finally with absolute alcohol, and air-dried. The residue was then rubbed up fine until all lumps were removed, and water carefully added, and a dough made of the mass. A tolerably coherent dough was thus obtained, but much less elastic and tough than that produced from the untreated flour. This dough was then washed with water on a sieve, using every precaution to obtain a gluten, but none was formed.

2. Again, 7.5 grams of very finely ground air-dried gliadin were mixed intimately with seventy grams of fine corn-starch and distilled water added. A plastic dough was thus produced, but it had no toughness. On adding a little ten per cent. sodium chloride solution, the dough became at once tough and elastic. This was then washed with great care on a sieve with cold water,

[1] *Am. Chem. J.*, 15, 392–471.

a little ten per cent. salt solution being added from time to time, but in spite of every precaution no gluten was obtained.

3. The following experiment shows that the gliadin used was capable of forming gluten when glutenin was present, and also that salts have a marked influence on the toughness of wheaten dough.

Two portions of flour, weighing 100 grams each, were taken, and after adding five grams of gliadin to one, both were made into dough with the same quantity of water. The two doughs presented marked differences; that to which the gliadin had been added was much tougher and more yellow than the other. They were then washed with water as long as starch separated. The gluten was dried superficially by wiping with a cloth and weighed in the moist state. That from 100 grams of flour to which five grams of gliadin had been added weighed 44.55 grams; that from 100 grams of flour alone weighed 27.65 grams. The moist glutens were dried at 110° to constant weight, and both yielded the same proportion of dry gluten; *viz.*, 34.6 per cent. The yield of dry gluten was accordingly, in the first case, 15.41 grams, and in the second, 9.56 grams. The difference, 5.85 grams, shows that the added gliadin was fully recovered in the gluten.

The above figures show that these proteids combine with about twice their weight of water in forming gluten. The fact that the added gliadin entered so readily and completely into the formation of gluten indicates that it exists in the seed as such and undergoes no chemical change during extraction and drying.

The properties observed in testing the separated gliadin show how it acts in forming gluten, and explain many of the points observed by others and attributed to a ferment action.

When treated with distilled water in small amount the fine ground air-dry gliadin at once forms a sticky mass which, on adding more distilled water, dissolves to a turbid solution. If, however, a very little sodium chloride is added to distilled water and this applied to gliadin that has been first moistened with pure water, a very coherent, viscid mass results which adheres to everything it touches, and can be drawn out into long threads. If the gliadin is moistened with ten per cent. sodium chloride

solution and then treated with a larger quantity of this solution, the substance unites to a plastic mass which can be drawn out into sheets and strings, but is not adhesive. From this it is evident why Ritthausen, in washing flours which gave a fluid gluten, obtainable only in small quantity and with great difficulty, found that the addition of calcium sulphate to the wash-water rendered the gluten much more coherent and easily obtainable. The gliadin is thus proved to be the binding material which causes the particles of flour to adhere to one another in forming a dough.

But the gliadin alone is not sufficient to form gluten, for it yields a soft and fluid mass which breaks up entirely on washing with water. The insoluble glutenin is probaby essential by affording a nucleus to which the gliadin adheres and from which it is not mechanically carried away by the wash-water.

It might be supposed that this insoluble glutenin, which so nearly resembles gliadin in composition, results from an alteration of the latter, brought about by the action of the mineral or other constituents of the seed or of the water. This is not probable, for the same amount of gliadin is extracted from flour directly by treating it with alcohol of 0.90 sp. gr., as is obtained from the gluten itself, and also the same amount is obtained after extracting the flour completely with ten per cent. sodium chloride solution, and then with alcohol.

The behavior of the gliadin towards ten per cent. sodium chloride solution shows why no gluten was obtained by Weyl and Bischoff from flour extracted with this solvent. The gliadin had under these conditions no ahhesive qualities, and therefore was unable to bind the flour into a coherent mass. If, however, the salt solution is added in small quantities, and the flour kneaded and pressed, the particles are brought together and then adhere tanaciously.

DEGRAS.[1]

By Charles S. Bush.

IN this country, the term "degras" is generally applied to the grease or fatty matter recovered from the water in which wool has been scoured; in various portions of Europe, the term

[1] Read before the Rhode Island Section, January 25, 1894.

is employed not only in connection with grease extracted from the waste-water of wool-washing establishments, but also to designate the oil or fatty matter recovered at chamois-skin manufactories.

It is my intention at this time to call your especial attention to degras of the first named type, which, I may say, has but one source; namely, the water in which wool has been scoured.

The process of producing or manufacturing degras (or so-called wool grease) is, comparatively speaking, a simple one and may be described as follows: The soapy liquid remaining in the scouring tubs or machines, after the wool has been scoured, is run off into a large shallow tank or pond and allowed to settle; the greater portion of the grease rises to the surface, but more or less adheres to the dirt and other foreign matter and is carried to the bottom. From time to time, the material which has accumulated at the bottom of the tank or pond is removed, and the grease, or a large portion thereof, is recovered. After the settling process is completed, the liquid is pumped into tanks and allowed to stand for a few days. The next step in the process is to add sulphuric acid. This withdraws the alkali used for washing the wool and breaking up the soapy emulsion, causes the grease and water to separate (this is commonly called "cracking the grease"). The contents of the tanks are then transferred to filter beds where the water is allowed to drain off, the grease and sediment being left behind in the filters. The filter beds may be composed of sawdust or other suitable material. The substance remaining in the filters is then transferred to pieces of bagging and shaped into flat packages. A large number of these packages are placed in power presses and steam applied in order to raise the temperature sufficiently to cause the grease to ooze out and flow into tanks provided for the purpose. Any water which may find its way into the presses will naturally pass into the tanks with the grease, but separation takes place at once and the hot degras, forming a layer on top, is readily drawn off into the barrels. After the degras has been allowed to cool, it is of about the consistency of soft tallow, and in such form is ready for market.

The color of the substance under consideration is yellowish-

brown; it has a disagreeable odor which is not easily described. This odor is due to two causes; first the presence of foreign substances, as dung and urine products, which are still present while the grease is being melted; second, the presence of certain volatile fatty acids which were present as potash salts in the wool, and, being soluble in the grease, remain with it after treatment of the emulsion with strong acid.

The individual character is given to wool grease by an interesting substance called cholesterin, the chemical formula of which is $C_{26}H_{44}O$. This substance is soluble in hot alcohol but precipitated in cold, in the form of tabular crystals somewhat resembling silver nitrate. As the extracted wool grease does not precipitate in the crystalline form, I think it is fair to infer that the cholesterin exists in the wool fat chemically combined with the fatty acid, and not in a state of mixture. Cholesterin is not saponifiable but it makes a most perfect emulsion, taking up 120 per cent. of water and remaining in that emulsive state for years; a sample in my possession is three years old and still shows no signs of separating.

Degras finds its chief use in the finishing of leather, superseding tallow for that purpose to a great extent, on account of the low price of the former and because of its penetrating and emollient nature. Degras is used to some extent in the manufacture of wool-oils, rope-oils, etc. Many persons have been led to believe that this waste material, which has polluted our streams and formed a subject for much discussion, is used extensively in the manufacture of soap. Some months since, an article appeared in one of our local newspapers from which I quote the following words: "In regard to finding a market for this material, I think it possible to sell it to almost any soap manufacturer. A large business is done in New York in this, and at a price of 2 to $2\frac{1}{2}$ cents per pound." To say the least, this newspaper statement is misleading. Degras has been used to a slight extent by a few soap manufacturers but the results have been anything but satisfactory. Cholesterin is unsaponifiable and a positive injury to the soap. It has no detersive properties and is undesirable as a "filler." There is no doubt that new outlets for this interesting product will be discovered eventually.

THE BORIC ACID WORKS AT LARDARELO.[1]

By Wm. P. Mason.

SO far as I am aware no recent description of these famous works has been given, and there is certainly wide-spread ignorance as to the best route by which to visit them. The most convenient starting point is Pisa, whence a train may be taken for Cecina at 6.10 A. M.

At Cecina one must change cars for the branch line going to Volterra. At Volterra station (not the town of that name, which lies some five miles away) a comfortable one-horse wagon, holding two besides the driver, may be hired for the round trip for ten francs. The regular post is to be avoided as it does not go far enough. The drive to Lardarelo will take two and a half hours, and the return journey will take about the same time. An evening train leaves Volterra station for Pisa. An attempt to pass the night *en route* would be attended with discomfort and is not recommended.

Unless the visitor be able to speak Italian an interpreter would be absolutely necessary.

The scenery between Volterra and Lardarelo, although hilly, can hardly be termed mountainous; and the soil, though poor in quality, is cultivated, olive plantations being seen in plenty. Altogether, the description of the approaches to the place, as depicted by the older authors, savors of a much more grim locality than the valley seen by the traveler of to-day—its infernal characteristics sink into nothingness when compared with the Yellowstone Park.

The dark color of the masses of friable serpentine on the hillsides, during the last mile of the drive, is the only reminder of the scenery as described by Muspratt, but wherever this rock occurs it does certainly give the surroundings "the appearance of having been burned."

Upon crossing a ridge within half a mile of the end of the journey, the boric acid plant, and its attendant village, suddenly come into view, and, with the numerous jets of native steam

[1] Read at the Baltimore Meeting, December 28, 1893.

rising from and among the buildings, the resemblance is very strong to a busy New England factory town.

All of the district now covered by the works was originally owned by the people of the neighboring ancient town of Monte Cerboli, but having been held by them as of little value, it was very cheaply obtained in 1818 by a poor young Frenchman (grandfather of the present Count Lardarel) who detected the presence of boric acid in the steam and who was shrewd enough to appreciate the value of his discovery.

He at first formed a company for the purpose of developing the property, but later acquired entire possession himself.

The boric acid, to the extent of one-tenth of one per cent., is contained in the native steam that issues from the earth through numerous orifices, all of which have been tubed to a greater or less degree.

These tubings are mostly of eight-inch pipe, and extend into the earth varying distances, some a few feet and others over three hundred. Certain of the fumaroles are entirely artificial, having been bored after the manner of artesian wells. The boring tool, when it reaches the steam zone, usually drops suddenly a yard or more, and immediately thereafter steam escapes with much force. The temperature of the issuing steam varies in the different outlets from 98°–140° C., and it rushes from the pipes with great noise and power.

Ordinary spring water is led into a circular brick cistern about thirty feet in diameter, and an eight-inch pipe, conducting natural steam passes through the cistern wall about one foot below the water surface.

The issuing steam, which impregnates the water with boric acid, causes a fountain of several feet in height to play in the cistern.

After an interval of twenty-four hours the contents of this cistern are piped into another similar one on a lower level, and are then subjected to a further injection of steam for an additional twenty-four hours, after which the solution passes to a square settling basin where a grayish mud, of exceedingly fine state of division, separates.

This mud, which contains more or less boric acid, is given

away to the country people who use it as an application for diseases of the hide occurring among sheep and cattle.

From the settling tank the boric acid water passes to evaporating pans (forty in number) made of lead. These pans are six feet wide, 150 feet long, and eight inches deep. They are slightly inclined, and are divided by small ridges two and a half inches high crossing them transversely every two feet. The liquid enters at one end and slowly flows over the step-like divisions to the other, the rate of inflow being made equal to that of evaporation.

When, in the judgment of the attendant, the concentration has been carried far enough, the flow is cut off and the hot, concentrated liquor is brushed out by brooms into crystallizing tanks, ten by thirty feet in size, and allowed to cool.

The deposited crystals of boric acid are removed by wooden scoops, drained in baskets, and the mother liquor is returned to the evaporating pans.

The crystals are spread upon a steam-heated drying floor protected by a shed-like building thirty by fifty feet in area, and when dry are placed in bins for storage. Shipment is made in casks holding about 1,000 pounds each. The heating of the evaporating pans and drying floor, in short heating of every description throughout the establishment, is by native steam.

About 200 hands are employed in the works, and the annual output is approximately 1,700 tons, all of which is shipped to England, *via* Leghorn.

Count Lardarel appears to have a careful eye for the welfare of his employees, as is evinced by the substantial manner in which the village is built, its cleanliness and the attempts made to adorn the streets. He was awarded a medal at the Paris Exposition for his contributions towards the betterment of social conditions, in addition to an award made for his manufactures.

The statement in our standard works of reference that "boric acid is recovered at both Monte Cerboli and at Lardarelo," is confusing, as they are practically one and the same place; and the dimensions given the artificial lagoons, "100 to 200 feet in diameter," is a great exaggeration.

RENSSELAER POLYTECHNIC INSTITUTE,
May, 1894.

THE COMMERCIAL VALUATION OF LEAD-TIN AND LEAD-ANTIMONY ALLOYS.[1]

By Joseph W. Richards, Ph.D.

LEAD-TIN alloys are used principally as soft solders, for coating terne plates and making "tin-foil." The amounts used annually for these purposes in this country may easily amount to twenty or thirty thousand tons, valued at some five million dollars. Since lead is worth about five cents a pound, and tin about twenty, the percentage of the latter fixes the value of the alloy; and since dishonest manufacturers are constantly trying to "cut grades" by shaving down the proportion of tin, consumers are constantly on the alert to detect such frauds. A quick, easy method of determining approximately the percentage of tin in such alloys becomes a valuable desideratum in such important industries. Accuracy to one per cent. is amply sufficient for all commercial purposes, because alloys conscientiously made by a careful manufacturer will vary that much from what they are intended to be if made by simply mixing given weights of the two metals.

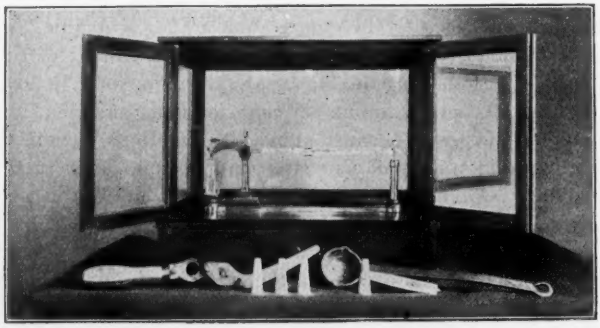
Lead-antimony alloys, or hard lead, run up to twenty-four per cent. of antimony. Many thousand tons of this is used annually in the type-metal and britannia-ware industries, the proportion of antimony varying usually between five and fifteen per cent.

The commercial testing and valuation of such alloys can be most conveniently and quickly accomplished by determining their specific gravities. Pure lead has a density of 11.33, pure tin 7.43, and antimony 6.65. When tin is added to lead, the density at once falls; not uniformly, however, and the alloy, furthermore, does not have a density such as could be calculated from that of its component metals. It is the same on adding antimony, except that with one per cent. the alloy is *heavier* than lead, with two per cent. it is just the density of lead, and above that figure the gravity decreases as with tin. Over twenty-four per cent. of antimony, no homogeneous alloy can be obtained, and this sets a limit to the specific gravity tests; however, twenty

[1] Read before the Lehigh Valley Section, May 3, 1894.

per cent. may be regarded as the maximum ever found in commercial "hard lead."

To inaugurate this scheme of testing, it is necessary to carefully make the whole series of alloys, every one or two per cent. from pure lead to pure tin, and from pure lead up to twenty-four per cent. of antimony. Having determined the specific gravity of these alloys by the time-honored scheme of weighing in air and water, with a good balance, the results are tabulated, and any commercial alloys similarly treated and referred to it are at once identified. This method, however, requires a delicate balance and a careful operator; in fact, rather more skill than an ordinary metal-handler possesses. The apparatus shown



in the accompanying cut was devised by Mr. Joseph Richards, of the Delaware Metal Refinery, Philadelphia, to facilitate these tests. The idea is to cast a bullet of fixed size in a brass mould, with each of the standard alloys, and then to weigh the bullets on a delicate scale. The scale shown has agate bearings, and the long beam is graduated every one per cent. from 0–pure lead, to 100–pure tin. On the reverse side, the beam is graduated from two up to twenty-four for the lead-antimony alloys. The marks on the beams have all been fixed by placing on the pan successively bullets of the standard alloys, and marking their weight.

The operation of testing a lead-tin or "hard lead" alloy thus resolves itself into simply melting it in a small iron ladle, pouring

the bullet and placing it on the scale; on balancing, the percentage of tin or antimony is read off directly on the beam. The balance is delicate enough to rise or fall with a movement of less than one-half of one per cent., while, with care, duplicate bullets may be cast not varying in weight over one-half per cent. The only precautions to observe are to continue the pouring until the bullet is set, in order to avoid a shrinkage cavity, and not to pour into a hot mould, which would necessarily be larger and cast a heavier bullet. The whole operation of melting, casting, and weighing can be performed easily in three to five minutes, and, if need be, by any workman of ordinary intelligence.

Nearly a score of these outfits have been sold by Mr. Richards during the last six months, and their introduction into the industries using these alloys has displaced the rule-of-thumb practice by accurate calculation, and brought many a dishonest manufacturer to his proper deserts.

PYROXYLIN, ITS MANUFACTURE AND APPLICATIONS.[1]

By Walter D. Field.

PART III.

(*Continued from p. 498.*)

THE peculiar form in which pyroxylin is deposited from its ether-alcohol solution, first called the attention of experimenters to it as a means for producing improvements in the various industrial arts. Photography was the first of the industrial arts to utilize this peculiar property of soluble nitrocellulose.

Later English experimenters made attempts to use pyroxylin as the base for an imitation bone, ivory or hard rubber. Parks, Spill, Greening, and others labored industriously to find some way or some solvent that would dissolve pyroxylin so they could obtain it in solid blocks suitable for turning and molding.

Four years after Scott Archer used pyroxylin in photography, Parks filed his first patent for the use of a solution of pyroxylin. (Eng. Pat. No. 2359, Oct. 22, 1855.) Then again in May, 1858 (Eng. Pat. No. 1090), John MacIntosh proposed the use of pyroxylin dissolved in a solvent composed "of equal parts of wood spirit and coal naphtha" for use in the insulation of wire. In 1864 Parks (Eng. Pat. No. 2675) proposed the use of pyroxy-

[1] Read before the World's Congress of Chemists, June, 1893.

lin with gum ballata and says: "I employ as a solvent which I prepared by distilling wood naphtha with calcium chloride." Parks seems to recognize the desirability of using a solvent as near anhydrous as possible, and says the greater the quantity of calcium chloride used the stronger the solvent. But because of his solvent Parks was unable to make his experiments successful, and so he begins to search for solvents that would not evaporate so quickly and would enable him to work the pyroxylin solution in heated rolls. Parks finds that nitrobenzene, aniline, glacial acetic acid, and camphor dissolved in the more volatile solvents, methyl alcohol and alcohol-ether are much better for use in producing a plastic as they are less volatile and develop greater solvent action under the influence of heat.

Spill (Eng. Pat. No. 3102, 1869) finds camphor in alcoholic solution, camphor oil, aldehyde alone or with alcohol, solvents of pyroxylin. Ethyl and methyl acetates were found to be solvents of pyroxylin by Pelouse (*Compt. rend.*, **24,** 2), and ether-alcohol by Dominte and Merard (*Compt. rend.*, **29,** 390). Acetone was known to be a solvent of pyroxylin prior to 1864. To the solvents already given none were added until 1882, when John H. Stevens took out a series of patents, in which he gives a large number of new solvents for use in the production of solid compounds of pyroxylin. In these patents (U. S. P. Nos. 269, 340, 269,341, 269,342, 269,344, 269,345,) he names the following substances: methyl nitrate, ethyl butyrate, ethyl valerate, ethyl benzoate, ethyl formate, methyl salicylate, amyl formate, amyl acetate, amyl butyrate, amyl valerate, ethyl sebacylate, ethyl oxalate, diamyl oxide, which are all active solvents of pyroxylin, that is they are solvents at the usual temperatures. He names dinitrobenzene and coumarin as latent solvents, that is, they are solvents at their melting points or when dissolved in alcohol. Stevens also finds acetal, amyl nitrate, and amyl nitrite in alcoholic solution to be solvents of pyroxylin at ordinary temperatures.

In 1889 Robert Shupphous took out a series of patents (U. S. P. Nos. 410,204, 410,205, 410,206, 410,207, 410,208, and 410, 209). He finds propyl and isobutyl alcohols with camphor active solvents, and the ketones, palmitone, and stearone in

alcoholic solution, also alpha and beta naphthol with alcohol, and anthraquinone (diphenylene diketone) in alcoholic solution. Iso-valeric aldehyde and its derivatives, amyliden-dimethyl and amyliden-diethyl ethers, Shupphous finds are active solvents of pyroxylin.

In 1892 August Sayer (U. S. P. No. 470,451) informs us that diethylketone, dibutylketone, dipentylketone, and the mixed ketones, methylethyl, methylpropyl, methylbutyl, methylamyl, and ethylbutylketones are active solvents of pyroxylin. Still later Leonard Paget (U. S. P. No. 494,793) finds that methyl-amyl oxide is a solvent but ethylamyl oxide (U. S. P. No. 494, 792) is not a solvent.

The solvents of pyroxylin can be divided into the following general classes: First, those which are solvents, without the aid of heat or solution in alcohol; second, those that are solvents when dissolved in alcohol. These solvents are those which also develop a solvent action when heated to their melting point in combination with pyroxylin.

We also find that chemically the solvents of pyroxylin can be grouped into classes as follows: Two of the monohydric alcohols; compound ethers of the fatty acids with monohydric alcohols; aldehydes; simple and mixed ketones of the fatty acid series. These classes include the greater number of the solvents of pyroxylin those not included are as follows: Amyl nitrate and nitrite, methylenedimethyl ether, ethidenediethyl ether, amyl chloracetate, nitrobenzene and dinitrobenzene, coumarin, camphor, glacial acetic acid, and mono, di, and triacetin.

Another division of the solvents of pyroxylin is necessary when we consider their properties. We find it necessary to divide the solvents of pyroxylin into two great classes according as they are hygroscopic or non-hygroscopic. To the first class belong acetone, methyl acetate, ethyl acetate, methyl alcohol, aldehyde, ethyl formate, propyl formate and acetate. These solvents when they deposit pyroxylin from their solution, also absorb water and this precipitates the pyroxylin in the form of a white cloud on the surface of the deposited film. In some cases this cloudiness extends entirely through the film and it is like chalk dust in appearance.

Dr. Guido Wolfram (*Dingler's Poly. J.*, **230,** 156,) says: "Pentanitrocellulose is soluble in acetone, acetic ether, and still easier in a mixture of the same with ethyl ether. The solution gives a cloudy layer (matte) or film on evaporation." The pentanitrocellulose was not the cause of the cloudy film, for if he had used anhydrous solvents and evaporated his solution in a chamber free from moisture he would have obtained clear films.

Wolfram says: "The solution of the tetranitrocellulose in acetic ether, acetone, and wood-spirit, wood-spirit ether, acetic ether, ether, and acetone ether, gave a hazy opaque layer—a proof that the obtaining of a vitreous layer depends not only on the substance but likewise on the kind of solvent used." If Wolfram had used alcohol instead of ether in combination with the hygroscopic solvents he would have obtained clear transparent or glassy films on the evaporation of the solvent by reason of the alcohol absorbing the water and preventing the precipitation of the pyroxylin.

All the non-hygroscopic active solvents of pyroxylin deposit it from solution as a transparent, glassy film.

The action of the various solvents towards pyroxylin is often very peculiar. Thus is the case of the alcohol-ether solvent, neither the ether nor the alcohol is a solvent yet when combined they produce an active solvent. Camphor when dissolved in alcohol produces a good solvent; on the other hand camphor dissolved in the ketones reduces their solvent action. Nitrobenzene gives a solution that is granular, it seems to merely convert the pyroxylin and not to dissolve it, on the addition of alcohol (distilled from lime) we have at once a solution, that is, the granular appearance disappears and the solution becomes homogeneous.

The acid mixture and the method of nitrating has much to do with the action of the various solvents. The influence of water (uncombined) in the acid mixture, the influence of the immersion temperature, and the effect of increasing the nitric acid and diminishing the sulphuric acid, all influence the solubility of the resulting product.

We will consider first the influence of mechanically mixed water on the solubility of the pyroxylin.

Starting with a mixture of eight pounds of nitric acid, sp. gr. 1.435, and sixteen pounds of sulphuric acid, sp. gr. 1.83, and one-twentieth part by weight of cotton, first add six ounces of water and immerse the cotton at 60° C. The cotton is finished in ten or twelve minutes, and when washed and dried is found to be very pulverulent, or rotten and dusty, and occupies a much smaller bulk than the non-pulverulent variety insoluble in methyl alcohol. This pyroxylin is very soluble in methyl alcohol and in all hygroscopic solvents, giving with them limpid thin solutions.

Again taking the same proportions of acids of the gravities as given above, and the same amount of cotton for nitration, and adding nine ounces of water, the temperature of the immersion this time being 65° C., we find the pyroxylin produced very much more soluble in methyl alcohol than that produced by the first formula. Also that all its solutions are more limpid or fluid.

In this formula we have the following amounts of water: Eight pounds nitric acid, sp. gr. 1.435, contains 2 pounds, $2\frac{2}{5}$ ounces water. Sixteen pounds sulphuric acid, sp. gr., 1.83, contains 1 pound, $1\frac{23}{25}$ ounces water. Nine ounces water added makes the total water in the acid mixture 3 pounds, $13\frac{8}{25}$ ounces.

Now if we took a weaker nitric acid that would contain the desired water, without addition, as in the following formula: Eight pounds nitric acid, sp. gr. 1.40, contains 2 pounds, $10\frac{4}{5}$ ounces. Sixteen pounds sulphuric acid, sp. gr. 1.83, contains 1 pound, $1\frac{23}{25}$ ounces. Giving a total of 3 pounds $12\frac{8}{25}$ ounces. We would naturally suppose that this formula, containing as it does within an ounce of the same amount of water as the first formula, would produce pyroxylin having almost identical solubilities with that produced by the first formula. The two formulas do not, however, produce pyroxylins having the same solubilities, using, of course, in nitrating, the same temperature.

The pyroxylin produced by the formula containing the mechanically added water, is very soluble in methyl alcohol and hygroscopic solvents, but only imperfectly soluble in non-hygroscopic solvents, for instance, the compound ethers. Whereas the pyroxylin produced by the second formula, containing no mechanically added water, is perfectly soluble in the non-hygroscopic solvents, and its solutions in the hygroscopic solvents

are inclined to be heavy. The nitric acid used in these experiments was water-white and free from any dissolved nitrogen oxides.

The pyroxylin made from the formula containing the mechanically added water yields a film that is very contractile, that is, when it is deposited from its solution on a piece of plate glass it differs from other pyroxylins in drying to a much smaller bulk.

It was, however, the fact that the non-hygroscopic solvents of pyroxylin would deposit it as a film having great strength and transparency that led to its use for producing a varnish which could be applied to brass and silverware by simply dipping articles in it. The person who practically applied these properties was Richard Hale (U. S. P., No. 471,422). Hale uses the following solvent: Amyl acetate, four volumes; petroleum naphtha, four volumes; methyl alcohol, two volumes; pyroxylin, four to five ounces to the gallon of solvent. In this case, Hale has used petroleum naphtha to hasten the drying qualities of the varnish, so that it would set on the article to be varnished before it had a chance to run off. It was, however, the non-hygroscopic character of the solvent that made the varnish successful when it came to practical application. This very formula, or one which is a very slight modification, is used to-day in the production of thousands of gallons of pyroxylin varnish.

The varnish made on this principle is also used for varnishing pens and pencils and it gives them such a superior finish that they command a higher price than those varnished with the ordinary varnish.

And now the last industry that has sprung up, because of the wonderful properties of pyroxylin when deposited from its solution in a non-hygroscopic solvent, is the production of photographic films, flexible glass we would call it, and really, what better name could we give it? Henry Reichenbach made the first application of the use of a solvent of pyroxylin, that was practically non-hygroscopic, to the production of a photographic film. In his patent, issued in December, 1889, Reichenbach gives a formula, but as this formula is no longer in use, from the fact of its being too largely composed of hygroscopic solvents, there is no need of producing it here. It has been due to the recognition

by experimenters, that by a suitable combination of solvents solutions could be produced that would flow fast or slow, set rapidly or slowly, and produce the varied products desired, that the industry has developed so rapidly.

Hyatt's discovery that a mixture of camphor and pyroxylin when heated could be worked like rubber was the beginning of the success of the celluloid industry. Hyatt discovered the latent solvent action of camphor.

RECENT WORK ON THE SUGARS.

By B. B. Ross.

Received May 14, 1894.

THE ESTIMATION OF INVERT SUGARS.

Bauman (*Ztschr. des Ver. f Rubenzucker Ind.*, **42,** 824) gives a new table, based upon the original table of Herzfeld, for the calculation of invert sugar percentages in solutions containing considerable proportions of sucrose. The table is quite similar to that of Herzfeld, but provides for the employment of only five grams of material instead of ten grams, as in the old table.

Ehrmann (*Bull. Assoc. Chim., France,* **10,** 537) describes a method for the indirect gravimetric estimation of glucose by means of the reduction of one of the double platinum chlorides by the copper suboxide thrown down by the invert sugar.

The suboxide, precipitated in the usual manner is brought upon the filter and washed thoroughly; the reduction of the precipitate is next effected by pouring upon the filter a small amount of a concentrated solution of potassium platino or sodium platinochloride, the red precipitate of suboxide being superseded by a black deposit of platinum.

After washing and igniting the residue, the amount of invert sugar corresponding to the weight of platinum obtained, can be readily calculated.

The author claims that this method is more rapid and easy of execution than the reduction of cuprous oxide in a current of hydrogen, and that it is also more exact, for the reason that the atomic weight of platinum is much higher than that of copper.

Nihoul (*Chem. Ztg.*, **17,** 500) refers to the gravimetric

method dependent upon the reduction of the copper suboxide in a current of hydrogen, and offers the objection that the process, though accurate, is both tedious and time-consuming.

The process of Holdefleiss, involving the oxidation of the cuprous to cupric oxide with nitric acid, is also noted, as well as the objection of Soxhlet that a loss occurs from the formation of basic copper nitrate and that an error is occasioned by the retention of copper in the filters. The author reports results of tests refuting the first claim of Soxhlet and recommends the employment of double filters in order to obviate the slight error resulting from the presence of the small amount of copper retained in the filter papers. The inner filter containing the precipitate, and the outer filter are separately treated with nitric acid, ignited and weighed, the differences in the weights secured giving the weight of cupric oxide, and this multiplied by the factor 0.889 gives the amount of cuprous oxide corresponding thereto. From this the proportion of glucose can be readily obtained by reference to Allihn's tables.

Blank experiments with double filters showed that practically the same amounts of copper solution were absorbed and retained by each filter.

On account of the passage of small quantities of the suboxide through the first filter (as sometimes happens), it is recommended that quadruple filters be employed, the filters being ignited and weighed in pairs instead of individually.

By the observance of these directions, it is claimed that satisfactory results can be quickly and easily secured.

The author also reports the result of experimental tests of the gravimetric method which provides for the bringing of the suboxide upon tared filters, drying and weighing.

Two sets of double filters were employed in the filtrations, and in order to determine whether or not oxidation of the precipitate occurred during the drying process, some of the precipitated suboxide was maintained at a temperature of 75°–100° C. for two days without perceptible variation in weight.

It was found on investigation, however, that the precipitate obtained did not correspond precisely, in composition, to the formula Cu_2O, being contaminated to a slight degree with organic matter.

In following this method, which in other particulars is said to be highly satisfactory, it is therefore necessary to make a correction for the proportion of organic matter contained in the precipitate, this correction being generally about 0.3 to 0.4 per cent. of the weight of the cuprous oxide.

INVERT SUGARS IN THE BEET.

Classen (*Deutsche Zucker, Ind., 1893, Sucr. Ind.*, **41**, 242) recommends that in the estimation of invert sugars in the beet, the juice obtained by pressure from the beet be not employed and that, instead, the direct aqueous method of extraction be used in the preparation of the solution required for the determination.

For this purpose, the warm digestion process is found advantageous, a small amount of lead subacetate and precipitated calcium carbonate being previously added. Excess of lead subacetate should be avoided since this leads to the destruction of invert sugars, and on the other hand, if the juice has an acid reaction, inversion of sucrose will take place; the acidity, however, can be readily corrected by the employment of calcium carbonate.

The process recommended is as follows: Take 110 grams finely divided chips, add ten to fifteen cc. lead subacetate solution and one to two grams of precipitated calcium carbonate, digest in a half-liter flask on a water-bath from three-quarters to one hour. After cooling and making up to the mark, the moderately clear juice is decanted off and 100 cc. of it is measured out; a small amout of lead subacetate is next added to complete the clarification and the solution made up to 110 cc. and filtered. To 100 cc. of the filtrate a small amount of soda solution is added to precipitate the lead and the volume is then brought up to 200 cc. One hundred cc. of this liquid corresponds to ten grams of the beet pulp, and after it's filtration, the reduction of Fehling's solution can be accomplished in the usual manner.

LEAD SUBACETATE FOR CLARIFICATION.

Courtonne (*Bull. Assoc. Chim., France*, **10**, 457) refers to the chief methods proposed for the preparation of lead subacetate solutions and to the various formulas which have been assigned to this salt.

A series of tables is presented, giving densities of solutions of neutral and basic acetate, with the proportions of the solid salt, lead oxide and acetic acid contained therein, and showing also the relations between the two classes of solutions with reference to the amounts of acid and base present.

The author proposes the preparation of a basic acetate solution by adding to a solution of the neutral salt, an amount of ammonia sufficient to combine with such a proportion of the acetic acid of the lead acetate as will result in the formation of lead subacetate in solution along with ammonium acetate.

The proportions of the substances employed in the preparation of this solution are as follows:

Crystallized neutral lead acetate	350 grams.
Distilled water	825 "
Ammonia (22°)	55 "

The author states that this solution has been employed by him for a long period of time and has given uniformly good results in the clarification of sugar solutions.

In addition to the tables above referred to, the author inserts an additional one giving data of a corresponding character for solutions prepared by the process just described.

THE INFLUENCE OF LEAD SUBACETATE UPON THE POLARIZATION OF CANE JUICES.

Saillard (*Bull. Assoc. Chim., France*, **10**, 354) reports results of a number of polariscopic tests of cane juices, where both normal and basic lead acetate were employed in the clarification.

Where the subacetate was employed the results were considerably higher owing to the formation of insoluble lead levulosate, thus decreasing the normal levo-rotary influence of the invert sugar present.

The author gives examples showing the effect of this difference upon the aggregate results for a whole milling season.

[Note by abstractor—Attention was called to this point a number of years since by Gill, Spencer, Edson, and others.]

THE INFLUENCE OF ALKALINE NITRATES UPON THE POLARIZATION OF SUGAR SOLUTIONS.

Gravier (*Bull. Assoc. Chim., France*, **10**, 351) reports a number of experiments which he has conducted in order to ascertain

the influence of alkaline nitrates upon the polarization of sugar solutions. The tests were executed with both aqueous and alcoholic solutions, and both in the presence and absence of lead subacetate.

In aqueous solution the influence of potassium and sodium nitrates was almost inappreciable, but in alcoholic solutions, in the presence of lead subacetate, there was quite a considerable diminution in the polariscopic readings.

The author concludes that it is inadvisable to employ alcohol as a solvent in polariscopic work, especially where lead subacetate is used.

[TO BE CONTINUED.]

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE ROSE POLYTECHNIC INSTITUTE.]

THE VOLUMETRIC DETERMINATION OF PHOSPHORUS IN STEEL.[1]

BY W. A. NOYES AND E. D. FROHMAN.

Received June 18, 1894.

VERY full directions for the volumetric determination of phosphorus in steel have been recently given by C. B. Dudley and F. N. Pease.[2] The method is rapid and easy of execution and gives concordant results in the hands of careful workers. There is, however, an uncertainty of about ten per cent. as regards the factor which should be used for converting the iron equivalent of the permanganate solution into the phosphorus equivalent. The most careful determination of the character of the products obtained by reducing molybdic anhydride with zinc and sulphuric acid seems to be that of v. der Pfordten,[3] who finds that when solutions are reduced and titrated with but slight exposure to the air the molybdenum is reduced to a form corresponding to the oxide Mo_2O_3. If this is true one molecule of molybdic anhydride requires, after reduction, the same amount of oxygen for oxidation as three atoms of iron. If we assume, further, that the yellow precipitate contains twelve molecules of molybdic anhydride for one atom of phosphorus, it follows that

[1] The work here described was presented to the Faculty of the Rose Polytechnic Institute for the degree of Bachelor of Science by E. D. Frohman.

[2] *J. Anal. Appl. Chem.*, 7, 108. This JOURNAL, 15, 519.

[3] *Ann. Chem.*, (Liebig) 222, 155.

one atom of phosphorus is equivalent to thirty-six atoms of iron. The iron equivalent of the solution should, therefore, be multiplied by $\frac{31}{36 \times 56}$, or by 0.01538, to find the phosphorus equivalent.

Werncke,[1] however, claims that the molybdenum is reduced to a form corresponding to the oxide $Mo_{12}O_{19}$. This would give the factor 0.01628.

Blair[2] follows Werncke and gives factors which reduce to the one last given.

Dudley and Pease[3] assume the same ratio between molybdic anhydride and iron but a different and empirical ratio between phosphorus and molybdic anhydride. Their factors combined give the factor 0.01724.

Doolittle and Eavenson[4] give factors which, when reduced to the same form, give the factor 0.0160.

These facts led us to take up a study of the question in order to determine, if possible, the cause of the differences and what the true factor is.

We undertook first the determination of the form to which the molybdenum is reduced. For this purpose we intended to use known amounts of pure molybdic anhydride. On examining the molybdic anhydride on hand, which had been bought as chemically pure, we found that it contained considerable quantities of ammonia and also some sodium. On account of the difficulty of preparing the anhydride in pure condition we determined next to use sodium molybdate. This was prepared from the anhydride by dissolving in the calculated amount of sodium hydroxide and crystallizing the salt obtained from water. When dried over sulphuric acid *in vacuo* the salt contains two molecules of water of crystallization. This is completely expelled at 250°.

0.5713 gram of the salt lost 0.0823 gram H_2O at 250°.

0.1710 gram of the salt lost 0.0249 gram H_2O at 250°.

		Found.	
Calculated for $Na_2MoO_4+2H_2O$:		I.	II.
$2H_2O$	14.88	14.40	14.56

1 *Ztschr. anal. Chem.*, **14**, 9.

2 "Chemical Analysis of Iron," first edition, p. 86.

3 This JOURNAL, **16**, 230,

4 Ibid, **16**, 243.

The purity of the dry salt was further established by determining the amount of sodium in it by gentle ignition in dry hydrochloric acid as described by E. F. Smith and Philip Maas.[1]

0.3620 gram of the dry salt gave 0.2044 gram NaCl.

0.1148 gram of the salt gave 0.0648 gram NaCl.

		Found.	
Calculated for Na_2MoO_4.		I.	II.
NaCl	56.70	56.46	56.44.

For reduction 4.3405 grams of this sodium molybdate, dried at 250°, were dissolved in 200 cc. of water. Ten cc. of the solution, therefore, contained 0.1517 gram of molybdic anhydride.

The permanganate solution used was standardized by means of ammonium oxalate and of ferrous ammonium sulphate.

0.8923 gram of the ferrous ammonium sulphate required 17.88 cc. of the solution.

0.2077 gram of the ammonium oxalate required 22.93 cc. of the solution.

These results give respectively 0.007129 and 0.007144 as the iron equivalent of the solution, and one cc. of the solution contains 0.00102 gram of available oxygen.

For reduction ten cc. of the solution of sodium molybdate referred to above were diluted with 140 cc. of water and fifty cc. of dilute sulphuric acid (1 : 5 by vol.), and the solution was passed through the "reductor"[2] and followed by 100 cc. of dilute sulphuric acid (1 : 100) for washing. The solution was then titrated in the flask. In all the experiments a correction was made for the amount of potassium permanganate required in blank experiments with the same quantities of dilute sulphuric acid. The corrected values are given throughout this paper.

In the first experiments amounts of potassium permanganate were required which corresponded to from 15.90 to 16.35 per cent. of oxygen as compared with the amount of molybdic anhydride present. If reduced to the form corresponding to the oxide Mo_2O_3 16.67 per cent. of oxygen should be required, while for the form $Mo_{12}O_{19}$ but 15.74 per cent. is required. The results were not concordant and a little study of the matter led to the discovery that the reduced solution is very easily reoxidized by

[1] This JOURNAL, 15, 398.

[2] *J. Anal. Chem.*, 3, 123.

exposure to the air or by oxygen contained in water used for dilution. We have since found that Werncke states this fact very clearly in his paper,[1] but his statement seems to have been overlooked by recent workers and curiously enough Blair states almost exactly the contrary.[2]

The following illustrations of the ease with which the solution is oxidized may be given. A solution reduced as usual and which would have required at least sixteen per cent. of oxygen for its oxidation was poured into a beaker and back into the flask several times and then required only 14.89 per cent. of oxygen. A second solution reduced and then poured back and forth six times required only 13.74 per cent. of oxygen.

As it is evident from these experiments that the reduced solution must be titrated with very little exposure to the air, the reduction was next effected as follows: ten cc. of the sodium molybdate solution were diluted with 140 cc. of water and fifty cc. of dilute sulphuric acid. In the flask which was to receive the solution were placed two grams of acid sodium carbonate and five cc. of dilute sulphuric acid, thus expelling the air almost completely. A small amount of very dilute sulphuric acid was passed through the reductor first, then the molybdate solution as described and then 100 cc. of water containing five cc. of dilute sulphuric acid for washing. During all, care was taken to keep the reductor full and allow no air to pass through it. The reduced solution was titrated immediately *in the reductor flask*. Two solutions reduced in this way required respectively 24.8 cc. and 24.83 cc. of the permanganate solution, or 16.74 per cent. and 16.76 per cent. of oxygen.

The use of acid sodium carbonate for ordinary work would be somewhat troublesome and we next tried the effect of expelling most of the air from the reductor flask by passing through the reductor sixty cc. of dilute sulphuric acid (1 : 30) and following this with the solution to be reduced and the acid wash-water, taking care throughout that no air entered through the reductor tube. Ten cc. of the solution of sodium molybdate diluted with 140 cc. of water and fifty cc. of diluted sulphuric acid (1 : 5),

[1] *Ztschr. anal. Chem.*, 14, 7.

[2] "Chemical Analysis of Iron," p. 89.

required, when reduced in this way, 24.81 cc. of the permanganate solution, or 16.74 per cent. of oxygen.

Experiments were next tried with pure crystals of ordinary ammonium molybdate. This has the composition $(NH_4)_6Mo_7O_{24}+4H_2O$, and should require if the molybdenum is reduced to the form corresponding to the oxide Mo_2O_3, 13.59 per cent. of oxygen for reoxidation; 0.2037 gram of the salt required, after reduction as last described, 27.48 cc. of the permanganate solution; 0.2025 gram of the salt required 27.32 cc. These amounts correspond to 13.76 and 13.76 per cent. of oxygen.

Some molybdic anhydride was next prepared by gently igniting in a porcelain dish a comparatively pure specimen until all ammonia was expelled and the substance had changed to a pure yellow color, 0.1722 gram of this anhydride required, after reduction as last described, 27.76 cc. of the permanganate solution and 0.1726 gram required, 28.23 cc. or 16.44 and 16.68 per cent. of oxygen.

These experiments prove conclusively that if the reduction is properly executed the molybdenum is reduced to the form corresponding to the oxide Mo_2O_3. The conditions are that the solution should be preceded by some dilute sulphuric acid so that most of the air in the reductor flask may be expelled before the reduced solution enters it, that the sufficiently dilute solution shall pass the reductor slowly[1] and be followed by the acid wash-water without allowing air to enter the reductor at the top, and that the reduced solution shall be titrated at once and *without further dilution*. The reduced solution should be of a pure green color and not olive-green.

After establishing the ratio between molybdic anhydride and iron for the permanganate solution there still remain two questions before we can consider the ratio between the iron and phosphorus as settled.[2] These are, what is the ratio between molybdic anhydride and phosphorus in the yellow precipitate, and is the precipitation of the phosphorus practically complete in the case of the small amounts usually present in a steel analysis?

[1] See Doolittle and Eavenson. This JOURNAL, 16, 241.

[2] The paper of Prof. S. W. Johnson (this JOURNAL, 16, 462) has appeared since this was written. The presence of aluminum or manganese in its precipitate would not affect the results of the volumetric method. Iron, if present, would affect the results and that point deserves a more careful study.

The fact that there are twelve molecules of molybdic anhydride for one atom of phosphorus has been so thoroughly established by different observers that it seems scarcely necessary to discuss the matter or even to cite authorities. The experiments of Dudley and Pease[1] can not be considered as having much bearing on this question when we consider the extreme difficulty of the gravimetric determination of such minute amounts of phosphorus and the facts with regard to the reduction of the molybdenum which have been considered above.

The question as to the completeness of the precipitation is more difficult but we believe it is best studied by the precipitation of solutions containing known amounts of phosphorus under conditions practically identical with those of the steel analysis.

A solution of sodium phosphate was prepared of such strength that one cc. contained 0.000102 gram phosphorus (determined by evaporating a measured volume of the solution, igniting and weighing the sodium pyrophosphate), three cc. of this solution were placed in a flask with five grams of ferrous sulphate, free from phosphorus (equivalent to about one gram of iron), nitric acid was added, then potassium permanganate, and the precipitation of the phosphorus was effected exactly as directed by Dudley and Pease. The precipitate, after washing, was dissolved and reduced as described in the first part of our paper. In duplicate experiments 3.08 and 3.0 cc. of permanganate were required, which gives 0.34 and 0.33 mgm. of phosphorus instead of 0.31 mgm. actually present, if we use the theoretical factor which we have deduced for the relation between iron and phosphorus. Dudley's factor on the other hand would give 0.37 and 0.38 mgm.

Determinations were also made of the phosphorus in three samples of steel containing known amounts of phosphorus which were kindly furnished us by Dr. Dudley. They are the same steels to which Dr. Dudley has already referred. We give the results of our analyses calculated by the theoretical factor obtained by multiplying the iron equivalent of the permanganate solution by 0.01538, and also by the empirical factor of Dudley and Pease.

[1] This JOURNAL, 16, 229.

	Gravity determination, Per cent.	Volumetric determination. By theoretical factor.	By factor of Dudley and Pease.
Steel No. 1.....	0.040	0.040	0.045
" "	....	0.040	0.045
" "	....	0.039	0.044
Steel No. 2.....	0.053	0.050	0.056
" "	....	0.052	0.058
Steel No. 3.....	0.032	0.029	0.032
" "	....	0.034	0.038
" "	....	0.032	0.036

It is evident that the theoretical factor gives results which agree closely with the gravimetric determinations while the results calculated by the empirical factor of Dudley and Pease are decidedly too high. The evidence that the precipitation of the phosphorus is practically complete is quite satisfactory. It will be remembered that steel No. 2 contains arsenic. Our results seem to indicate that the arsenic is not precipitated to an appreciable extent with the phosphorus.

If the theoretical factor for the ratio between the iron and phosphorous equivalents of a potassium permanganate solution shall be confirmed by other observers, as we feel confident that it will be, the volumetric determination will be placed on so firm a basis that, at least in the absence of arsenic, the results obtained by it must be considered as more reliable than those obtained by any gravimetric method now in use. This cannot be true so long as the determination depends on an empirical factor, for any empirical factor is likely to vary with the amounts of phosphorus present and would not be applicable to steels containing widely different amounts of phosphorus.

TERRE HAUTE, June 15, 1894.

THE ANALYSIS OF MALT.

BY TOM CROSSMAN.

Received June 18, 1894.

IN the JOURNAL for May, 1894, there is an article on the analysis of malt by Dr. Miller. As a few of Dr. Miller's statements are totally opposed by those who have given the chemistry of malt their life study, I feel justified in bringing before your readers the methods of analysis which are in use for the valuation

of English malts in all our large breweries. The methods being based on the splendid researches of O'Sullivan, Heron, Brown, Morris, and others. I am aware that for the English infusion mashing we require better malt than when practicing the German decoction system. No doubt the methods given by Dr. Miller would give satisfaction to those brewers working on the German principle; but I make bold to assert, that a malt tested by the methods given in the article referred to, would not give information to the brewer which would be of any great practical guidance to him.

Dr. Miller asks, "From the standpoint of the brewer, the largest consumer of malt, what are the most important points to be ascertained by the analysis of a malt?" He then gives them as follows:

1. Moisture.
2. Extract.
3. Diastatic power.
4. Acidity.

I may add that the above factors *do not* tell the brewer much; but when taken in conjunction with the following, the results give him information of the greatest possible value.

5. Ready-formed sugars, soluble in cold water.
6. The percentage of uncoagulable albuminoids, soluble in cold water.
7. The quantity of free maltose, malto-dextrins, and free dextrin, when the malt is mashed under standard conditions.
8. The amount of unmodified starch or steeliness.

With reference to No. 1, nothing need be said as far as the method is concerned; but no practical brewer would ever dream of using malt containing five per cent. of moisture. Malt having three per cent. is generally looked upon with suspicion if required for a stock ale. One per cent. is normal to a good well-cured, and properly stored article.

The determination of moisture does not in all cases give us the information whether the malt has been properly dried or not originally, since it might have gained the water during careless storage. No brewer of my acquaintance thinks of judging the price of malt by the amount of water it contains, since he

knows fully well that the increase in moisture means increased deterioration.

2. The extract is usually determined by English chemists by what is known as Heron's method.[1] It consists of mashing fifty grams of ground malt with 400 cc. of water at 68° C., and keeping the temperature of the mash at 65°–66° C. for one hour. Afterwards the mash is cooled to 15.5° C. and made up to 515 cc. (500 cc. water, 15 cc. for space occupied by grains). The gravity is taken and the extract calculated therefrom. The wort is reserved for the further analysis, 7.

Heron's method is one which has given great satisfaction, since it is possible to analyse the starch products and compare them with other malts, giving information which is very much appreciated by practical brewers. The method is, by far, preferable to that following the conversion with iodine.

As opposed to Dr. Miller's statement I find that the majority of ale brewers are more guided, when purchasing malt, by the *quality* of the extract, as determined by the tests I am enumerating, than by the *quantity*.

3. The diastatic capacity is best determined by Lintner's method, which gives us the amount of curing the malt has been subjected to. It must not be forgotten, however, that two malts, each having the same diastatic power, will not behave the same, even if mashed under identical circumstances, unless the starch in each is in the same state of friability or freeness. Since, if the one malt is hard and vitreous and the other is free, the diastase will have more "work" to perform in the former than in the latter; therefore, the relative amounts of free maltose and malto-dextrin will be quite different. This is a point overlooked by several, they thinking if malts contain a given quantity of diastase, all the starch conversions will be the same providing the temperatures are similar. This is not so. The estimation of the diastatic power is not of much use unless we know the condition of the starch as determined by 7 and 8.

4. The acidity needs no comment.

5. The percentage of ready-formed sugars convey to the brewer more information as to the quality of the malt than is generally

[1] The Polariscope and Its Application to Brewing, (*J. Soc. Chem. Ind.*, 7, 259–276).

supposed. If the amount is low it is evident that the barley has been insufficiently germinated. If the quantity is high (*i. e.* over seventeen per cent. calculated on the malt) brewers agree that the beer produced from such a malt will not be sound; it also goes to prove that the malt has been forced or too quickly grown on the floors at high temperatures.

6. The amount of uncoagulable albuminoids and the amount of ready-formed sugars seem to bear a relation to each other. Moritz[1] has published some very interesting experiments which go to prove that under conditions specially favoring the attack and transformation of starch into sugars, there is a similar specially active attack upon the original albuminoids, and an abundant transformation of them into soluble forms. He also publishes a number of analyses of malts, and in each case he gives the factor obtained by dividing the soluble albuminoids into ready-formed sugars. It is a most noticeable fact that this factor is either 6.3, or a figure closely approximating it. There is sufficient proof here to convict the most skeptical, that it is absolutely impossible for a chemist to estimate the value of malt without first determining, 5 and 6.

7. By the estimation of free maltose and malto-dextrins, we get the knowledge how the starch is converted into the different sugars. It supplies to the brewer more information than it is at first possible, by non-brewers, to conceive; since it informs him how the starch behaves at fixed temperatures and conditions, he can then, to suit the class of beer he is desiring to produce, arrange his mashing heat with a certain amount of reliability.

Dr. Miller says, "It has been claimed by some that the percentage of sugars formed, and the amount of proteids dissolved, is of importance in judging the character of malt." I claim that the amount of sugars formed is very important in judging the character of malt, provided all malts are mashed under standard conditions, as is done when using Heron's method. I am aware that the increase or decrease of the percentage of the various transformation products is entirely dependent upon the manner in which malt is handled in the mash-tub, *combined with the condition of the starch and the amount of diastase*. Therefore, if the

[1] Technical Brewing; a Report on the Chief Features, in the year 1893.

brewer gets information as to the amount of the various sugars a malt yields when mashed under known conditions, surely he has a sound foundation upon which he can base his ideas in guiding him in the manner which the malt should be handled in the mash tub. The amount of free maltose and malto-dextrin in a wort, determine, to a very large extent, the condition, flavor and attenuation of the resultant beer. I cannot sufficiently emphasize the great importance of these determinations to the practical man.

8. The amount of unmodified starch or steeliness.

This a test of some significance, but not generally practiced. Its advantages are that it gives us the amount of unmodified or vitreous starch. It will be as well if I state the objects of malting, so as to better illustrate the importance and advantages of this test. The principal objects of malting are: The dissolution of the cellulose forming the cells in which the starch granules are enclosed, and the consequent liberation of the starch; the breaking down of the nitrogen constituents of the corn; the production of diastase for the future service in the mash-tub. Now, when the original barley is bad, or the malting has not been carried out on proper lines, the cellulose surrounding the starch granules is not dissolved, the starch is "locked up," so to speak, and in a very refractory condition making it well nigh impossible for the diastase to convert it at ordinary temperatures. A large amount of starch is then left in the grains, which may possibly get "semi-dissolved" and partly washed out by the subsequent higher sparging heats, and not being converted makes the production of gray or hazy beer very easy. If it were only a matter of dealing with steely malt we could surmount the difficulty by the decoction system of mashing; but it is understood that when the dissolution of the cellulose forming the cells is not satisfactory we have evidence of the glutens being only partly modified, and the resultant beers will not be as brilliant as those produced by a fully modified malt. Thus, a malt gives the best results in practice when the amount of unmodified starch, as estimated below, is small, providing other conditions are favorable. The following is the method I have used the last two years and have found exceedingly useful:

Fifty grams of malt are mashed, as in 2; the mash is then boiled very vigorously for one hour and afterwards cooled to 150° F. Fifty cc. of a cold water extract, previously prepared, as described below, are now added; the mash is kept at 150° F. for one hour longer. It is now cooled down to 60° F. and made up, as in 2, to 515 cc. The gravity is taken, allowance being made for the gravity added, *i. e.*, fifty cc. cold water extract. The difference in solid matter between boiled mash and mash, (2), will give the amount of unmodified starch. Example:

Boiled mash	77.0	per cent. solid matter,
Mash (2)	70.0	" " " "
	7.0	" " of unmodified starch.

The following is, in my opinion, the manner in which the results of malt analyses should be stated.

COMPOSITION OF WORT MASHED UNDER STANDARD CONDITIONS.

Free maltose, fermentable	33.30
Ready-formed sugars, fermentable	14.08
Malto-dextrins, unfermentable { maltose, 3.0 / dextrin, 1.9 }	4.90
Free dextrin, unfermentable	13.40
Albuminoids	2.21
Ash	1.60
Acid as lactic acid	0.51
Total dry extract	70.00
Unmodified starch	7.00
Moisture	1.90
Grains	21.10
	100.00

Diastatic capacity	30.
Color of wort	pale.
Flavor	good.

When the amount of unmodified starch exceeds much over seven per cent. it is sufficient to regard the malt with suspicion. A remarkable thing and an undisputed fact is, that beer made from a good foreign malt is more sound and brilliant than when made from good English malt. Yet, on comparing the analysis of each, we find that the unmodified matter, ready-formed sugars and soluble albuminoids, are smaller in amount in the foreign

than in the English malt. This speaks volumes for the value of malt analysis when conducted as described above.

NOTE.—Preparation of cold water malt extract. Fifty grams of ground malt are added to 500 cc. cold distilled water, and allowed to stand four hours with frequent stirring. It is then filtered absolutely brilliant, and used as directed.

THE LABORATORY, ALBION BREWERY,
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ON THE REACTION BETWEEN MOLYBDIC ACID AND POTASSIUM CHROMATE AND BICHROMATE.

BY ROBERT H. BRADBURY.

Received June 21, 1894.

MOLYBDENUM, as its position in the periodic system of the elements would indicate, offers many analogies with sulphur and more particularly with chromium. Thus, the most important acid of each is H_2RO_4, and the most stable acid-forming oxide RO_3. Again, sulphur and chromium have for some time been known to form a higher unstable oxide R_2O_7, and more recently a hydrated Mo_2O_7 has been prepared and investigated.

Potassium bichromate, $K_2Cr_2O_7$, is more fully written $K_2CrO_4CrO_3$, that is, it consists of a molecule of the neutral chromate combined with a molecule of chromic anhydride, and still higher anhydrochromates, *e. g.*, potassium trichromate, $K_2Cr_3O_{10}$ or $K_2CrO_4 2CrO_3$, have been shown to exist. The marked likeness between molybdenum and chromium led to the supposition that it might perhaps be possible to replace the chromium in potassium bichromate by molybdenum—that is, to obtain a compound $K_2CrO_4.MoO_3$. Since the bichromate results by the direct addition of chromic anhydride to the neutral chromate, it was supposed that the hypothetical chromo-molybdate might result by simple addition of molybdic anhydride to potassium chromate, thus

$$K_2CrO_4 + MoO_3 = K_2CrO_4.MoO_3.$$

At the suggestion of Dr. Smith I have investigated this subject, and while the result is not what was expected, it is of interest as adding another to the long list of facts which show that the rôle played by a substance in a reaction depends not only on the special qualities of the substance, but also to an equal degree on the amount in which it is present. The reaction which ensues when molybdic anhydride is brought together

with chromates has been investigated: A in the case of potassium chromate, B with potassium bichromate.

A. In determining the reaction of molybdic anhydride with neutral potassium chromate, the salt was dissolved in water and an equivalent quantity of molybdenum trioxide was added in small portions. Whether in the cold or in warm solution the molybdenum trioxide rapidly dissolves, the solution at the same time turning deep yellow-red in color. The molybdic oxide dissolves more rapidly when the process is executed in warm solution. The liquid was then slowly evaporated. At first there separated out from the solution a white mass. It was filtered, dried, and examined. It contained no chromium and was chiefly made up of unaltered molybdenum trioxide, perhaps with some potassium molybdate. The filtrate, which still retained its reddish-yellow tint, was evaporated. Further separation of the white material was constantly observed. From time to time it was again filtered off and the evaporation continued. At length a filtrate was obtained which was small in bulk and which apparently contained no more of the molybdic acid. In this, the reddish-yellow color which has already been referred to, was much deeper, corresponding with the increased concentration and showing that none of the colored material had been removed by the filtrations. This liquid was evaporated to crystallization and allowed to stand. The mass of red needles which separated was dried and recrystallized. This material was then examined. Under the microscope it did not differ from potassium bichromate, either in crystallization or in behavior toward polarized light. Analysis revealed the presence of but a trace of molybdenum and allowed no further doubt as to its nature.

The reaction between potassium chromate and molybdic anhydride therefore proceeds in the sense of the following equation:

$$2K_2CrO_4 + MoO_3 = K_2Cr_2O_7 + K_2MoO_4.$$

No direct addition takes place and no chromo-molybdate is produced. It follows from the fact that much unchanged molybdic anhydride separated out during evaporation and that the liquid contained a great deal of unaltered potassium chromate that the reaction is by no means quantitative. In fact the amount

of potassium bichromate formed is exceedingly small relatively to the quantities of potassium chromate and molybdic anhydride employed. Indeed we should expect from the position of molybdenum in the periodic system, from its higher atomic weight and from all the properties of its acid that the avidity of molybdic acid would be much less than that of chromic acid and therefore that the reaction

$$2K_2CrO_4 + MoO_3 = K_2Cr_2O_7 + K_2MoO_4$$

would not proceed very far before the stage of equilibrium would be reached in which the backward reaction

$$K_2Cr_2O_7 + K_2MoO_4 = 2K_2CrO_4 + MoO_3$$

attains the same velocity as the principal one and in which therefore the transformation ceases.

It would be possible, probably, to increase the quantity of potassium bichromate formed by increasing the amount of molybdic anhydride until a large excess of it was present, but no experiments in this direction have been made.

B. When molybdic anhydride is introduced into a solution of potassium bichromate in the cold no change appears to occur, but no experiments beyond a rough test have been carried out in this direction. The reaction which was investigated between potassium bichromate and molybdic acid takes place only at higher temperatures. Equivalent quantities of potassium bichromate and molybdic anhydride were mixed together and heated gently in a porcelain crucible. The mixture melts rather easily to a blackish-brown liquid and at the same time an effervescence, escape of oxygen, is noticed, which becomes more energetic as the temperature is raised. When the fusion became quiet the lamp was removed. On cooling, the contents of the liquid solidified to a brown mass, which was broken up and treated with hot water. Some unchanged bichromate was removed by this procedure and the insoluble residue was thoroughly washed and dried. It is a soft, loose powder of brown color. It was then subjected to analysis.

Hydrochloric acid dissolves most of it to a green solution, giving off chlorine. A small quantity of black residue remains which is not affected by nitric acid, or by nitric acid and potassium chlorate, or by fusion with sodium carbonate and sulphur.

On this account this residue was simply dried on a weighed filter and its weight deducted from that of the substance taken.

The process of analysis may be briefly described. The material was weighed out into a beaker, addition of sufficient strong hydrochloric acid to cover it was made and the heat of a water-bath applied. After complete decomposition, the residue, invariably slight in amount, was filtered off on a weighed filter and its weight deducted from that of the substance taken. The green filtrate was largely diluted with water and hydrogen sulphide passed into it for a long period. Molybdic trisulphide (MoS_3) precipitated. It was filtered on a weighed filter and its weight determined. An aliquot portion of the precipitate was taken and ignited in a Rose crucible in a strong current of dry hydrogen to convert it into molybdenum disulphide, MoS_2. The heat applied here must not be too high, or part of the material volatilizes yielding a black sublimate and loss of weight is the result. The molybdenum disulphide was allowed to cool in the current of gas and then weighed, and the quantity of molybdenum corresponding to the whole of the precipitate and therefore to the substance taken was found by the appropriate calculations. From the filtrate the chromium was precipitated as hydroxide by the addition of ammonia and was estimated in the usual way as sesquioxide.

The potassium in the filtrate from the chromium was weighed as usual, as chloride.

The results follow:

	A.	B.	C.	Mean.
Mo	43.69	43.56	43.17	43.45
Cr	14.71	14.65	15.00	14.79
K	11.08	....	11.86	11.47
Oxygen by difference				30.29

The formula $K_2O.Cr_2O_3.3MoO_3$ requires the following composition:

Mo	42.42
Cr	15.44
K	11.51
O	30.63

The compound in question is thus a basic molybdate of chromium and potassium.

UNIVERSITY OF PENNSYLVANIA,
June, 1894.

ACTION OF MOLYBDENUM DIOXIDE UPON SILVER SALTS.

By Edgar F. Smith and Owen L. Shinn.

Received June 15, 1894.

IT has been shown (*Ztschr. anorg. Chem.*, **1**, 360) that metallic molybdenum precipitates metallic silver from ammoniacal argentic solutions, but no record seems to have been made of the fact that molybdenum dioxide behaves similarly. This, however, was observed to be the case on introducing dioxide, prepared by the reduction of trioxide in a current of hydrogen, into an aqueous argentic nitrate solution for the purpose of learning whether any metal was present in the dioxide. All of the material dissolved on the application of a gentle heat. The solution was especially rapid in the presence of a slight quantity of ammonia. The silver separated in crystalline leaflets. Attempts were made to discover whether the reaction was really quantitative. The results are as follows:

1. 0.1057 gram brown dioxide, prepared by the reduction of ordinary molybdic acid in an atmosphere of hydrogen, precipitated from a slightly ammoniacal argentic nitrate solution 0.1755 gram metallic silver.

2. 0.1772 gram of dioxide precipitated 0.2915 gram of metallic silver. The latter was washed with dilute ammonia and with water.

Thinking that possibly the dioxide as prepared for the preceding precipitations did not really represent that oxide, but a mixture of oxides, recourse was had to a method first suggested by Manro and Pauebianco (*Gazz. chim. ital.*, **11**, 501). Muthmann (*Annalen der Chem.*, **238**, 116) employed this method with success. It is, briefly, the fusion of eight grams of dehydrated ammonium molybdate, seven grams of molybdic acid, fourteen grams of ignited potassium carbonate and seven grams of boric acid in a capacious and well-covered platinum crucible. The mixture should be held for several hours in a liquid condition. On cooling, a brittle mass results; it contains crystals of the dioxide. It can be readily detached from the crucible. The

brown oxide was purified by washing with ammonia water and then with pure water. The two reductions made with this oxide resulted as follows:

3. 0.3698 gram of oxide precipitated 0.6250 gram of silver.

4. 0.5287 gram of oxide threw out 0.8799 gram of silver.

In both cases ammonia, sufficient to precipitate silver oxide and again dissolve it, was added to the argentic solutions. The precipitated silver was also washed with ammonia water and finally with pure water.

If the ratio between the dioxide and the silver be deduced from the figures given in the preceding experiments it will be found to approach

$$1MoO_2 : 2Ag,$$

and then the calculated or theoretical quantity of silver required for the dioxide used in the various experiments would be

	Calculated Ag.	Found Ag.
1	0.1783 gram.	0.1752 gram.
2	0.2990 "	0.2915 "
3	0.6240 "	0.6250 "
4	0.8765 "	0.8799 "

The results in 3 and 4 agree more nearly with the theoretical requirements than those in 1 and 2, doubtless because the oxide used in those experiments was a true molybdenum dioxide. Their variation from the theory may be ascribed in 3 to slight solubility of the precipitated metal in ammonia, and in 4 to minute traces of molybdic acid in the silver.

Additional trials were made to arrive at more concordant results, but success was not achieved, although in every instance the resulting silver approximated the ratio previously established. This reaction, while apparently useless for quantitative purposes, is yet of interest as it shows that the precipitation of metallic silver is not confined to metallic molybdenum, but that it even extends to the dioxide and perhaps to other mixed oxides of which the dioxide may be a part.

It is of interest to note in connection with the conduct of molybdenum dioxide as outlined in the preceding paragraphs, the further analogy established between it and the dioxides of other metals of Group VI. Thus, tungsten dioxide reduces not only copper and mercuric salts, but also precipitates metallic

silver from ammoniacal silver solutions, and uranium dioxide, prepared by reduction of the oxalate in a current of hydrogen, dissolves in silver nitrate with the separation of metallic sliver. Molybdenum dioxide showed no reducing action upon copper and mercuric salt solutions.

Among the non-metals of Group VI we observe in the deportment of sulphites towards silver nitrate, in the breaking down of silver sulphite into metallic silver on the application of a gentle heat, a behavior analogous to that exhibited by molybdenum dioxide, and which we may consider as an additional contribution to the many already well-established analogies, existing among the derivatives of the elements constituting Group VI of the Periodic System.

UNIVERSITY OF PENNSYLVANIA,
June, 1894.

NEW BOOKS.

PRACTICAL INSTRUCTIONS IN QUANTITATIVE ASSAYING WITH THE BLOWPIPE. CONTAINING ALSO READILY APPLIED QUALITATIVE BLOWPIPE TESTS. BY E. L. FLETCHER. pp. 142. 14 Illustrations. Price, 12 mo. cloth, $1.25; morocco, $1.50. New York: John Wiley and Sons. 1894.

The manual of blowpipe analysis contains 142 pages with numerous cuts showing apparatus. It is well printed on serviceable paper and is of convenient size to be carried in the pocket.

Chapter I consists of descriptions of apparatus and general directions for their use, also in some cases the price of special appliances.

Chapter II is devoted to reagents, those commonly used in assaying, etc.

Chapter III contains descriptions of the various colored coats and flame tests given by the volatile elements.

Chapter IV describes the colored beads produced by all of the common and many of the rare elements when dissolved in borax or salt of phosphorus, both with the oxidizing and reducing flames.

Chapter V gives the method of reducing oxides on charcoal with soda.

Chapter VI. This chapter is the best in the book; here the ordinary qualitative blowpipe tests are distinctly and succinctly described.

Chapter VII, Quantitative assaying, describes in considerable detail the operations of sampling and of making quantitative blowpipe assays for silver, gold, lead, copper, tin, mercury, nickel, cobalt, and bismuth.

The appendix contains tables of hardness, atomic weights, etc.

A defect in the book is that the weights of ore are given in grains while the divisions on the scale, used for measuring the size and hence determining the weight of the buttons, reads milligrams, thus making calculations necessary which would be simplified by the use of the assay ton system.

In regard to the accuracy of the results obtainable by the methods described, granting that the button can be measured accurately to a cross-line of the scale, the differences are so great as to render the method nearly useless for ordinary gold ores. Cross-line No. 1=18 cents a ton in gold, No 2=$1.40 a ton, No. 3=$4.80 a ton, No. 4=$11.60 and so on.

The book may prove useful to prospectors, skilled in the use of the blowpipe, who have the good fortune to discover rich veins. E. H. M.

MINERAL RESOURCES OF THE UNITED STATES CALENDAR YEAR 1893. BY DAVID T. DAY, 8 vo. pp. v, 810, Washington, D. C.: Government Printing Office. Price 50 Cents.

This annual volume so well known to those interested in the mining industry carries forward the statistics to Dec. 31, 1893, and gives much descriptive matter to a later date. The following statements are of especial interest to chemists:

Aluminum.—"The total production of aluminum reached 333,629 pounds. * * It can be said that nearly all the steel makers use a small proportion of aluminum with the result of less waste in castings. For example, the amount of waste in crop ends on steel rails is lessened profitably. Ingot aluminum also goes to manufacturers of aluminum cooking utensils and this industry is extending satisfactorily. The remainder of the product goes out as sheet and wire for many purposes including

numberless experimental uses, among them lithographing with aluminum plates instead of zinc or lithographic stone. Some experiments in this direction in the map department of the Geological Survey indicate that the transfers obtained on aluminum are superior to those on zinc."

Salt.—"Notwithstanding the low prices which have prevailed and which have been due to keen competition among producers, there has been a laudable endeavor on the part of a number of manufacturers to improve the quality of their product. In this, signal success has been attained, and salt of American production has been so improved by new processes, which each producer holds secret, that importations of refined salt have almost ceased to be a factor in the industry. The competition in the production of fine grades of salt has become as sharp in its way as the competition in prices. Table and dairy salts are now prepared for commerce practically chemically pure—free from gypsum, calcium chloride, and magnesium salts."

Space will not permit of further extracts from this useful volume. E. H.

SEVENTH ANNUAL REPORT AGRICULTURAL EXPERIMENT STATION OF NEBRASKA FOR THE YEAR 1893. pp. 206. Lincoln, Nebraska: State Journal Co. 1894.

The volume includes brief statements of the work of the year by the director and the heads of the different departments, a list of books in some of the sections, the usual roster of officers and the financial statements. With these are bound nine articles which have already appeared as station bulletins and the title page of one other.

Chemists will be most interested in the two articles on the culture of the sugar-beet by Prof. Nicholson and his assistants, and in the article on the influence of changes of food and temperature on the quantity and quality of the milk of dairy cows.

The work on the sugar-beet is planned to cover the subject thoroughly, including culture, yields, richness of the beet, value of rejected portions, study of physiological problems, effect of fertilization, cost of production, seed production, and injury from insects.

Since Nebraska has become the second beet-sugar producing state in the union, parties interested in the subject naturally look to the bulletins of the Nebraska station for reliable information on the subject. They will find much important matter in this report. The work has been carried out on a larger scale than is usual in experiment station work. Under the head of fertilizers for beets it is stated that the use of "guano" seemed to be injurious to the beet. It is to be regretted that the actual composition of this "guano" is not given, as the "guano" now sold is often very different in origin and composition from the guano of standard reference books.

All the articles are fully illustrated by cuts, plates, and charts which add very materially to the interest and value of the volume. H. A. HUSTON.

ELECTRO-CHEMICAL ANALYSIS. BY EDGAR F. SMITH. pp. 139, 27 illustrations. 2d Edition. Price $1.25. Philadelphia: P. Blakiston, Son & Co. 1894.

It is to Germany that we are accustomed to look for the scientific thoroughness which characterizes this little volume. Prof. Smith has long been known as an indefatigable worker in the field of electrolysis, and is a frequent and regular contributor to its literature. In this manual he presents, in clear and precise language, all that has stood the test of experience, and he deserves praise for avoiding to give undue prominence to his own methods. The very interesting chapter which he devotes to an historical sketch of the subject will doubtless serve to dispel erroneous notions that are entertained by many chemists regarding the authorship of certain methods.

In this new edition the character of the original work is preserved, but the additions show that the author has not allowed any recent publications of importance to escape his attention. Amongst others we note references to the interesting work of the Munich Polytechnic School, the valuable experiences of Elbs and of Oettel, and especially the excellent work that has been done in the laboratory of the University of Pennsylvania since the appearance of the first edition.

There is, no doubt, that we have here the most accurate, as well as the most complete work that has been written on electrochemical analysis. H. F. KELLER.

THE ALCHEMICAL ESSENCE AND THE CHEMICAL ELEMENT. AN EPISODE IN THE QUEST OF THE UNCHANGING. BY M. M. PATTISON MUIR. pp. 94. London: Longmans, Green & Co. 1894. Price $1.50.

This essay is a study "of the endeavors that men have made to give definiteness to the conception of unity of material phenomena" in the domain of chemistry. The discoveries and theories of the alchemists are summed up with no lack of appreciation, and the author proposes to judge the value of alchemical conceptions by finding "what results flowed from applying these conceptions to the study of nature." What, secondly, has chemistry accomplished by "examining material changes accurately and critically?"

The answers are given with dignity and fairness. The book is interesting; it seems intended for, and is adapted to the use of intelligent people who are not chemists, and contains home thrusts at some who are called "Modern Alchemists."

NINTH GENERAL MEETING OF THE AMERICAN CHEMICAL SOCIETY.

CIRCULAR OF ANNOUNCEMENTS.

THE Ninth General Meeting of the AMERICAN CHEMICAL SOCIETY will be held in Brooklyn, N. Y., on Wednesday and Thursday, August 15th and 16th, 1894. The first session will be held at 10 A. M., August 15th, in room 42 of the Polytechnic Institute, No. 99 Livingston street. After the session, at 1.30 P. M., it is expected that a steamer will leave one of the wharves of the East river taking the chemists to the New York side where a lunch will be served at the mineral water establishment of Mr. Carl H. Schultz. After lunch there will be an opportunity to inspect the manufactory, and then the steamer will proceed to the U. S. Artillery School at Willet's Point, stopping at intermediate places of interest, and returning to Brooklyn in the evening.

The morning session on Thursday will begin at 9 A. M., and later in the day visits will be made to manufactories in the vicinity, returning in time for the address of Vice-President Norton before Section C of A. A. A. S., at 4:30 P. M.

Invitations have been received to visit various chemical establishments and places of scientific interest, and the local committee will arrange for such visits at convenient times during the two days appointed for the meeting of the American Chemical Society and the remaining days of the week, as the chemists who remain to participate in the meetings of the A. A. A. S. will undoubtedly be glad to avail themselves of such opportunities. The local committee of arrangements for the meetings of the A. A. A. S., and the other bodies which will be in session in Brooklyn at or near the same date, have secured for all of these organizations railroad rates of one and one-third fare for the round trip to Brooklyn or New York and return, under the following conditions:

(1) Each person, in order to secure said rates, must purchase a first-class ticket to Brooklyn or New York and pay full fare therefor, obtaining from the ticket agent a certificate to that effect upon a regular printed form. Such certificates will be available from August 10th—five days before the opening of the meeting. In case the agent at the starting point is not supplied with certificates or cannot give through tickets, the regular fare must be paid to the nearest station where such certificates can be obtained.

(2) These certificates must be deposited by holders, on their arrival at Brooklyn, with the Local Secretary, Prof. Geo. W. Plympton, who will return them when desired for the return trip.

(3) Before presenting these certificates at the ticket office in Brooklyn for obtaining return tickets they must be filled in on the back by the Local Secretary and also countersigned by the Special Agent of the Trunk Line Association. The Special Agent will be in attendance August 16th, 18th, 20th, and 24th.

(4) Certificates and return tickets are not transferable and the certificates will not be received by the Ticket Agents in Brooklyn after August 31st.

ALBERT C. HALE,
Gen. Sec'y of the American Chemical Society.